



12-1987

Investigation of the Synthesis and Polymerization Behavior of Vinyl Benzoate

Selim Mehmet Erhan
Western Michigan University

Follow this and additional works at: <https://scholarworks.wmich.edu/dissertations>



Part of the Polymer Chemistry Commons

Recommended Citation

Erhan, Selim Mehmet, "Investigation of the Synthesis and Polymerization Behavior of Vinyl Benzoate" (1987). *Dissertations*. 2213.

<https://scholarworks.wmich.edu/dissertations/2213>

This Dissertation-Open Access is brought to you for free and open access by the Graduate College at ScholarWorks at WMU. It has been accepted for inclusion in Dissertations by an authorized administrator of ScholarWorks at WMU. For more information, please contact wmu-scholarworks@wmich.edu.



**INVESTIGATION OF THE SYNTHESIS AND POLYMERIZATION
BEHAVIOR OF VINYL BENZOATE**

by

Selim Mehmet Erhan

**A Dissertation
Submitted to the
Faculty of The Graduate College
in partial fulfillment of the
requirements for the
Degree of Doctor of Philosophy
Department of Chemistry**

**Western Michigan University
Kalamazoo, Michigan
December 1987**

**INVESTIGATION OF THE SYNTHESIS AND POLYMERIZATION
BEHAVIOR OF VINYL BENZOATE**

Selim Mehmet Erhan, Ph.D.

Western Michigan University, 1987

The goal of this study is to present a method that gives higher conversions and molecular weights for the polymerization of vinyl benzoate than obtained in previous investigations.

Polyvinyl benzoate has benzene rings attached to the backbone chain, therefore is hard and rigid. This is a characteristic which has a large application area. However previous studies in polymerizing vinyl benzoate with bulk and solution polymerizations reported low yields and troublesome crosslinking, which has limited its application. Emulsion polymerization method has the advantage of giving high polymerization rates together with high molecular weights, and therefore was chosen as the method for polymerization for vinyl benzoate in this study.

For the most suitable laboratory synthesis of vinyl benzoate, the vinyl interchange reaction between vinyl acetate and benzoic acid was used.

In emulsion polymerizations, emulsifiers and initiators have important effects on polymerization rates and molecular weights. Therefore different emulsifier and initiator systems were tried to find an emulsion polymerization recipe that would give high

conversions and high molecular weights. These efforts were successful and a recipe that gives 95% conversions in two hours at 75°C is reported. However molecular weights were somewhat low and further research in studies of recipes with a decrease in the amount of chain transfer agent is suggested.

The rate studies of the emulsion polymerization of vinyl benzoate revealed that increasing the initiator concentration increased the rate as expected. However there was an uncertainty in the increase of rate with increasing emulsifier concentration. Therefore for a better understanding of the polymerization behavior of vinyl benzoate, a more detailed study is recommended to determine the relationship of the number of free radicals in the polymer particle and the functionality of the particle number, N , to the initiator and emulsifier concentrations.

To aid the studies in the physical applications of polyvinyl benzoate, its absorption spectra, refractive index increments, viscosity average molecular weights for different recipes, its cohesive energy density and its film forming characteristics are also reported.

INFORMATION TO USERS

The most advanced technology has been used to photograph and reproduce this manuscript from the microfilm master. UMI films the original text directly from the copy submitted. Thus, some dissertation copies are in typewriter face, while others may be from a computer printer.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyrighted material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each oversize page is available as one exposure on a standard 35 mm slide or as a 17" × 23" black and white photographic print for an additional charge.

Photographs included in the original manuscript have been reproduced xerographically in this copy. 35 mm slides or 6" × 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.



Accessing the World's Information since 1938

300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA

Order Number 8804711

**Investigation of the synthesis and polymerization behavior of
vinyl benzoate**

Erhan, Selim Mehmet, Ph.D.

Western Michigan University, 1987

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark ☒.

1. Glossy photographs or pages _____
2. Colored illustrations, paper or print _____
3. Photographs with dark background _____
4. Illustrations are poor copy _____
5. Pages with black marks, not original copy _____
6. Print shows through as there is text on both sides of page _____
7. Indistinct, broken or small print on several pages ☒
8. Print exceeds margin requirements _____
9. Tightly bound copy with print lost in spine _____
10. Computer printout pages with indistinct print _____
11. Page(s) _____ lacking when material received, and not available from school or author.
12. Page(s) _____ seem to be missing in numbering only as text follows.
13. Two pages numbered _____. Text follows.
14. Curling and wrinkled pages _____
15. Dissertation contains pages with print at a slant, filmed as received ☒
16. Other _____

U·M·I

To

George G. Lowry

Robert C. Nagler

Sevim Z. Erhan

ACKNOWLEDGEMENTS

I would like to thank Western Michigan University and the Chemistry Department for the financial support and teaching experience gained from my teaching assistantship.

I would also like to thank Dr. R. C. Nagler and Dr. M. C. McCarville for all their moral support and help they provided throughout the many problems I encountered.

I remain indebted to my committee members, Dr. R. Janes, Dr. R. E. Harmon, Dr. J. A. Howell and Dr. H. D. Warren for their helpful suggestions, care and time they have devoted for the completion of this study.

I want to express my gratitude to my wife, Sevim, for the help she has provided without which I would not be where I am today.

I am also grateful to Joan Vroegop for her skillful help in preparing this manuscript.

Most of all I wish to express my sincere appreciation to Dr. G. G. Lowry for his helpful suggestions, patience, understanding, guidance, advice and critical eye that not only brought this investigation into perspective but also made it a very valuable experience for me.

Selim Mehmet Erhan

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	ii
LIST OF TABLES	vi
LIST OF FIGURES	vii
CHAPTER	
I. INTRODUCTION	1
Selection of Vinyl Benzoate	1
Synthesis of Vinyl Benzoate	2
Polymerization of Vinyl Benzoate	6
A Survey of Polymerization Techniques	7
History of the Polymerization Studies on Vinyl Benzoate	12
Emulsion Polymerization	16
Emulsifiers	17
Initiators	20
Other Additives	22
Experimental Approach Used in This Study	23
II. EXPERIMENTAL PROCEDURE	24
Materials Used	24
Polymerization	26
General Procedure	26
Exploratory Preparations	28
Rate Studies	30

Table of Contents -- Continued

CHAPTER

II. EXPERIMENTAL PROCEDURE	
Properties of Vinyl Benzoate and its Polymer	31
Dilute Solution Viscosity	31
Spectra	34
Refractive Index Increment	35
III. RESULTS AND DISCUSSION	37
Emulsion Polymerization of Vinyl Benzoate	37
Initiator Systems	38
Emulsifier Systems	45
Rate Studies	47
Properties of Polyvinyl Benzoate	54
Molecular Weight	54
Cohesive Energy Density	60
Refractive Index Increments	66
Absorption Spectra	66
SUMMARY AND CONCLUSIONS	74
RECOMMENDATIONS	77
APPENDICES	80
A. Polymerization Recipes	81
B. Viscosity Measurements of Polyvinyl Benzoate for Deter- mination of Molecular Weights in Methyl Ethyl Ketone at 30°C	93

Table of Contents -- Continued

CHAPTER

APPENDICES

C. Intrinsic Viscosities of Polyvinyl Benzoate Obtained from Recipe 65 at 32.5°C for the Determination of Cohesive Energy Density	99
D. Conversion versus Time Plots of Kinetic Experiments at 60°C	103
REFERENCES	114

LIST OF TABLES

1. Emulsion Polymerization of Vinyl Benzoate Using Potassium Peroxydisulfate as an Initiator	39
2. Emulsion Polymerization of Vinyl Benzoate Using Cumene Hydroperoxide as an Initiator	40
3. Emulsion Polymerization of Vinyl Benzoate Using Various Initiator Systems	41
4. The Effect of Changing Temperature, Emulsifier Type and Concentration in the Emulsion Polymerization of Vinyl Benzoate	43
5. The Effect of Increasing Sodium Hydrogen Sulfite Concentration on the Conversion in the Emulsion Polymerization of Vinyl Benzoate	44
6. The Effect of Changing Temperature and Emulsifier Concentration on the Emulsion Polymerization of Vinyl Benzoate	45
7. The Effect of Temperature and Emulsifier Type on the Emulsion Polymerization of Vinyl Benzoate When Potassium Peroxydisulfate is Used as an Initiator	46
8. The Effect of Temperature and Emulsifier Type on the Emulsion Polymerization of Vinyl Benzoate When Potassium Peroxydisulfate and Sodium Hydrogen Sulfite are Used as an Initiator System	47
9. Molecular Weights of Selected Polyvinyl Benzoate Samples	58
10. Intrinsic Viscosities of Polyvinyl Benzoate in Solvents Having Different Solubility Parameters	63
11. Refractive Index Increment of Polyvinyl Benzoate	66

LIST OF FIGURES

1. The Effect of Changing the Emulsifier Concentration at 75°C	50
2. The Effect of Changing Initiator Concentration at 75°C .	51
3. The Effect of Changing the Emulsifier Concentration at 60°C	51
4. The Effect of Changing Initiator Concentration at 60°C .	52
5. The Intrinsic Viscosity Determination of Polyvinyl Benzoate From Recipe 65 at 32.5°C in Acetone	56
6. The Change in the Slope of η_{sp}/C vs C with Changing η_{rel} Values, at 30°C, for Polyvinyl Benzoate Obtained From Recipe 70	59
7. The Solubility Parameter of Polyvinyl Benzoate	63
8. The UV Absorption Spectrum of Polyvinyl Benzoate Obtained From Recipe 69	67
9. The NMR Spectrum of Vinyl Benzoate	67
10. The NMR Spectrum of Polyvinyl Benzoate Obtained From Recipe 40	69
11. The NMR Spectrum of Polyvinyl Benzoate Obtained From Recipe 43	70
12. The NMR Spectrum of Polyvinyl Benzoate Obatined From Recipe 69	71
13. The IR Spectrum of Vinyl Benzoate	72
14. The IR Spectrum of Polyvinyl Benzoate Obtained From Recipe 69	73

CHAPTER I

INTRODUCTION

Selection of Vinyl Benzoate

Vinyl benzoate monomer as seen from its formula, $\text{C}_6\text{H}_5\text{COOCH}=\text{CH}_2$, resembles vinyl acetate, $\text{CH}_3\text{COOCH}=\text{CH}_2$, but has a phenyl ring in place of a methyl group. When the monomer is polymerized these will add rigidity to the chain. Research of the past work done on this polymer revealed that not only is it a hard, brittle, crystal clear resin (first observed by Ham and Ringwald¹), but it also gave crosslinked gels during polymerization and was slow to polymerize compared to some other monomers, like vinyl acetate, that have similar structures.

Most of the studies on vinyl benzoate had been done during the years when polymerization studies were rapidly expanding, and rewarding industrial applications were of greater interest. Therefore, this monomer had not been studied extensively, because of the problems mentioned in the last paragraph.

As properties like hardness and rigidity in a polymer can increase the areas of its usefulness, and as large industrial applications require efficient, low cost and high yield synthesis methods, a study of methods that might increase the effectiveness of the polymerization of vinyl benzoate would be rewarding. Motivated by this idea, first the synthesis of the monomer was studied.

Synthesis of Vinyl Benzoate

The idea behind the synthesis research was to find a fast, efficient and high yield process that could be applied to manufacturing large amounts of monomer.

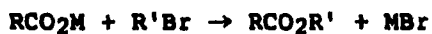
Most of the methods that can be applied to the synthesis of vinyl benzoate involve either very expensive catalysts or too many steps and long process times. However, there are a few that may be used in industrial applications.

Merker and Scott² have suggested a method in which the esters are obtained with a nucleophilic replacement reaction shown below, with yields often in the range of 70%.



This method involves reflux and separation and purification by distillation processes. Tertiary amines are preferred because primary and secondary amines might react with alkyl halides to form secondary and tertiary amine hydrohalides. However vinyl halides have a very low reactivity in nucleophilic substitution reactions. So with this method, even if the reaction occurred yields would be very low.

Another somewhat similar synthesis by Berlin and coworkers³ uses metal salts (Ag, K, Na) of carboxylic acid with alkyl halides represented by the following reaction.



These reactions were run in benzene or cyclohexane, and excess salt and metal halides were filtered off, followed by purification steps which would involve distillation of excess solvent. This type of synthesis also requires the preparation of the metal salt which produces extra steps, extra reagent use and storage problems together with stability problems, not to mention the generation of large amounts of byproducts.

Hennion and Nieuwland suggested a method⁴ to obtain vinyl esters using the reaction of acetylene with carboxylic acids. Although this method has not been tried for vinyl benzoate, it should be possible to synthesize it with the following general reaction:



However, there are side reactions giving anhydrides and aldehydes.

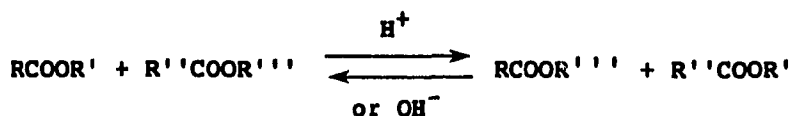


Boron trifluoride as the ether compound $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{BF}_3$ is used as a catalyst.

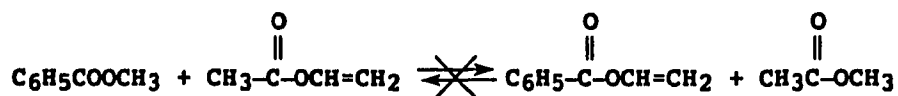
Again this method involves careful separation and purification of the product, and the yields for many synthesized compounds were in the range of 30-60% due to side reactions.

Vinyl interchange is one of the methods that has been studied extensively during the past years with the addition of many improvements. The name "vinyl interchange" is given to differentiate it from typical ester interchange and ester-acid interchange

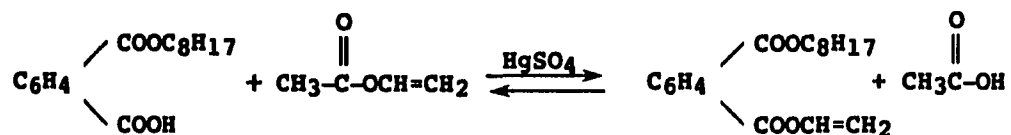
reactions⁵. The well-known interchange between two different carboxylic acid esters, such as shown below, has not been successfully carried out when one of the esters is a vinyl ester.



For example, in the reaction of methyl benzoate and vinyl acetate⁵ the expected product, vinyl benzoate, could not be obtained.



Again in the reaction of mono-octyl phthalate and vinyl acetate, shown below, only the carboxylic acid group reacted to give an ester and the octyl group was not replaced by the vinyl group.

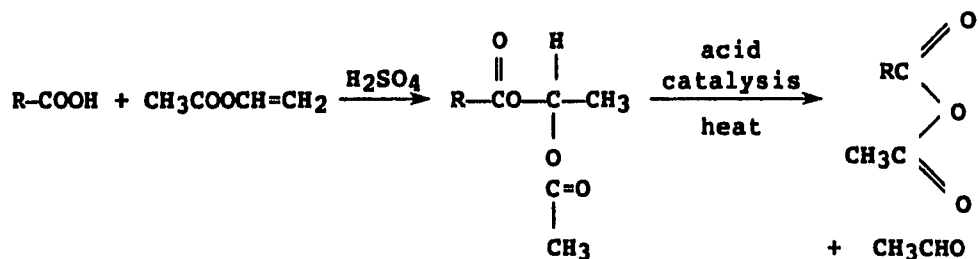


In the vinyl interchange reaction, very mild conditions and low yields of by-products lead to high yields of monomers, mostly above 70%. First reported by Hermann and Haehnel⁶, and Toussaint and MacDowell⁷, the reaction follows the general equation shown below:



Vinyl acetate and benzoic acid are refluxed with catalytic amounts (less than 2% of the mass of vinyl acetate) of mercuric acetate and sulfuric acid, and vinyl benzoate is distilled from the reaction

mixture. However care must be taken when monitoring reaction temperature and time, because above 75°C the reaction gives ethylidene diesters as by products. In that case, in order to get good yields another step is required, in which the ethylidene diesters are decomposed back to free acids.⁵



There have been studies to improve the vinyl interchange method of Hermann and Haehnel,⁶ using different catalysts. In one such system a palladium compound is used as a main ingredient and an alkali metal compound is a co-catalyst. Either the alkali metal compound or the palladium compound must be a halide.⁸ The catalyst system is then adsorbed on a solid catalyst carrier. According to this method the problem of decomposition of the palladium compound, encountered in the prior methods^{9,10} where chelated and unchelated palladium salts were used as catalysts, was almost completely eliminated, and the catalyst could be used repeatedly without the troublesome recovery of metallic palladium. Also when the catalyst ingredients are used as adsorbed on a solid catalyst carrier, so that the reaction is performed by heterogeneous phase catalysis, the repeated use of the catalyst would be more simplified.

However, in spite of all the improvements made to reduce the tremendous cost of the catalyst, still the reaction times are about 70 hours which encourages a search for other methods.

Currently the most efficient methods are gas phase reactions that have very short contact time and very high yields. For example benzoic acid and acetylene are passed over zinc acetate catalyst on activated carbon, between 250°-260°C entry temperature and 300°C over the catalyst with three second contact time to give yields of 90% or better of vinyl benzoate.¹¹

Fischer and Frytag¹², and Lussi¹³ reported similar results with cadmium acetate in place of zinc acetate. Again these yields and methods were verified by Heinman and Schmidt¹⁴, who also stressed the absence of side products and the ability to recycle excess acetylene. The results of the literature research shows that the industrial processes have a considerable superiority over the laboratory synthesis in respect to process time and yield of product. This research therefore will concentrate on the improvement of the polymerization of vinyl benzoate.

Polymerization of Vinyl Benzoate

The objective of this study is to give some more information on the polymerization behavior of vinyl benzoate which in the past has been polymerized with different techniques.

A Survey of Polymerization Techniques

There are four conventional categories in polymerizations; bulk, solution, heterogeneous and emulsion polymerizations.¹⁵⁻¹⁸

In bulk or mass polymerization, the only phase initially present is the pure liquid monomer itself, in which a small amount of initiator, chain transfer agent, etc. may also be dissolved. The polymer formed usually is soluble in monomer. In this case the liquid becomes extremely viscous after a portion of the monomer has polymerized. If the reaction proceeds too far, the polymer may be extremely difficult to remove from the vessel. Even well before this stage is reached, the high viscosity, together with the accompanying increased difficulty of agitation, results in poor dissipation of the heat of polymerization, so the interior portions of the mass may become quite hot. The heat build-up, of course, leads to an increased rate of polymerization. Bulk polymerization is of commercial importance particularly for the production of solid polymers with specific shapes.

In solution polymerization the monomer is dissolved in an appropriate solvent and polymerization is brought about by the addition of an initiator.

Heterogeneous polymerization can be divided into two subcategories: precipitation and suspension.

In precipitation polymerizations the polymer formed is insoluble in the reaction medium. Polymerization of acrylonitrile in water solution is an example.

In suspension polymerization the monomer is suspended as small droplets in a medium, generally water, where the monomer is insoluble. Protective colloids, or suspending agents, are used to keep the droplets, and later the polymer particles, from coalescing. The most important of these suspending agents are finely divided inorganic precipitates, such as magnesium phosphate, or water soluble high polymers, such as gelatin. Sometimes water-soluble salts are also used, like sodium chloride. These serve to lower the interfacial tension, increase the density of the aqueous phase, and decrease the solubility of the monomer in the aqueous phase. Increasing the density of the aqueous phase can be extremely important in industrial processes because if the density of the continuous phase is kept between the densities of the monomer and the polymer, agitation can be reduced and smaller amounts of protective colloids will be sufficient. It is essential to avoid the use of more than a trace of certain protective colloids, such as soaps, which are also capable of associating in the form of micelles and form an emulsion rather than a suspension.

Agitation forces the monomer droplets into contact with each other. The function of the suspending agent is to prevent the droplets from coalescing when they collide. It is this tendency of sticky droplets to coalesce, with the ultimate formation of a large lump of coagulum, which accounts for the fact that suspension polymerization is used only in the production of plastics and fibers, but not rubbers, which remain sticky throughout most of the polymerization. With suitable control, it is possible to produce beads

or pearls within a wide range of diameters. Therefore, the suspension technique is of great industrial importance.

From a kinetic standpoint suspension polymerization is identical with bulk polymerization. The advantages of suspension polymerization are ease of heat transfer, the low viscosity of the suspension, and the production of beads or powders that may be suitable for direct application. The chief disadvantage has been the somewhat lower purity of the product, which may remain contaminated with traces of surface active suspending agents.

The fourth major polymerization technique is emulsion polymerization. Here the monomer is emulsified in a medium, generally water, with the aid of emulsifying agents such as soaps. The monomer is present initially mostly as emulsion droplets dispersed in a continuous phase, water, but with a small amount of monomer inside soap micelles. Free radicals, formed in the aqueous phase from the initiator, diffuse into the monomer phase in the micelles and initiate polymerization. As polymerization proceeds the micelles start to swell as monomer diffuses in from the emulsified droplets. Additional monomer diffuses into the polymer and the polymer keeps growing until another free radical enters the micelle and terminates the growing chain.

After a certain point in the polymerization, emulsifier molecules are no longer in the form of micelles but coat the surface of the polymer droplet and prevent it from coalescing. Actually as more and more surfactants are adsorbed onto the surface of the

polymer, their concentration drops below the critical micelle concentration. At this time the role of agitation becomes more important, because in the absence of agitation the polymerizing monomer droplets can coalesce. The polymerization continues after this point until nearly all the monomer is depleted. At 100% conversion the size of the polymer particles, typically between 50 and 200 nm, will be between the sizes of the initial micelles (usually between 2 and 10 nm) and the initial monomer droplets (about 1000 nm).

The disadvantages seen in suspension polymerization can also be seen in emulsion polymerization. For instance if a solid polymer is desired, it must be expected that contamination with surface active agent and other water-soluble ingredients will be particularly serious owing to the extremely high surface area of the very small particles. In products where high clarity or very good electric insulation is needed, this becomes a very big drawback because the traces of soap, salts or water will have adverse effects on these properties.

However, heat transfer presents no difficulties since the viscosity of the emulsion remains low during the change to latex. The combination of the highly effective surface active agents, very mild agitation and small size of polymer particles minimizes the tendency of the particles to coalesce, making emulsion polymerization suitable for the production of sticky, rubbery polymers. The product is a latex, which is suitable for many direct applications.

One of the principle advantages of emulsion polymerization is the possibility of forming a polymer of high molecular weight at a very high rate of polymerization. In bulk or solution polymerization at a given temperature a growing polymer molecule adds monomer units at a definite rate. The rate of polymerization per gram of monomer is therefore proportional to the number of growing polymer molecules. However, the rate of termination is proportional to the square of the concentration of growing polymer molecules, since the growth of these molecules is terminated by collision with one another. Therefore, attempts to increase the rate of polymerization by increasing the concentration of free radicals, also increase the rate of termination, and lead to the formation of polymers of lower molecular weight. The rate of polymerization is found to be proportional to the square root of the rate of initiation, and the number average molecular weight of the polymer is inversely proportional to the square root of the rate of initiation.

In a typical emulsion polymerization system the latex consists of a large number of very small particles of polymer, with an average diameter of a few tenths of a micron, suspended in water. The solubility of the monomer in the polymer is such that each polymer particle is swollen with approximately an equal amount of monomer. Free radicals are not formed within the particles, but enter from the surrounding water phase in which the initiator is dissolved. When a free radical enters a particle, polymerization is initiated and continues until it is terminated by the entry of another radical into the particle. Thus it is possible for a

molecule to grow to a very high molecular weight before it is terminated. This growth can proceed simultaneously in a large number of particles since they are isolated from each other by the intervening water phase, and a growing polymer molecule in one particle cannot terminate its counterpart in another particle. The overall rate of polymerization is therefore high. Actually the molecular weights in emulsion polymerization are often so high that it is necessary to add a modifier to regulate the molecular weight.

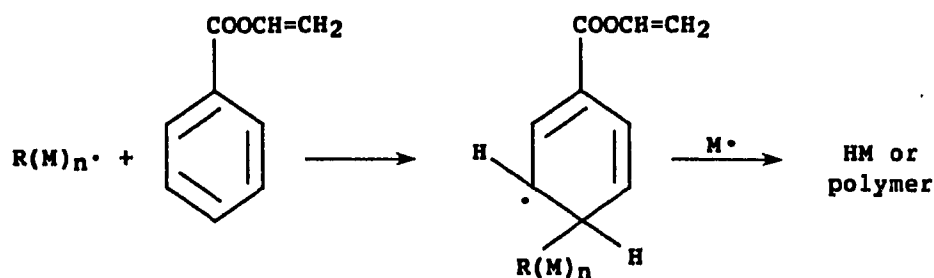
History of the Polymerization Studies on Vinyl Benzoate

In the past vinyl benzoate has been polymerized in bulk and in solution. The first polymerization and copolymerization studies done by Ham and Ringwald¹⁹ showed that bulk polymerization of vinyl benzoate produces a cross-linked, hard, brittle, and crystal clear resin. This observation was confirmed by the studies of Morrison, Gleason and Stannett,²⁰ Burnett and Wright,²¹ Santee and coworkers,²² and Banarjee and Muthana.²³ These studies indicated that the monomer possibly had a bifunctional character; for example, the radicals generated might have added to the benzene ring forming a resonance-stabilized radical that only participated in termination reactions.

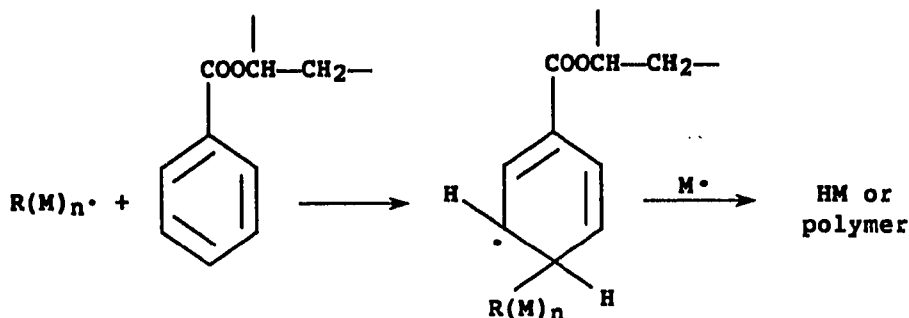
Kinetic studies, done by Morrison, Gleason and Stannett,²⁰ and by Burnett and Wright,²¹ revealed that the overall rate of polymerization was proportional to the square root of the initiator concentration, and termination reactions occurred by binary collisions of free radicals. It was also established that the

reaction was first order with respect to monomer concentration, which signifies an initiation process independent of monomer concentration.^{22,23} Furthermore they stressed the importance of meticulously purifying the monomer, by pointing out that the cause of previous disagreements about the kinetics and retardation mechanism^{20,21} was due to impurities in those monomers.

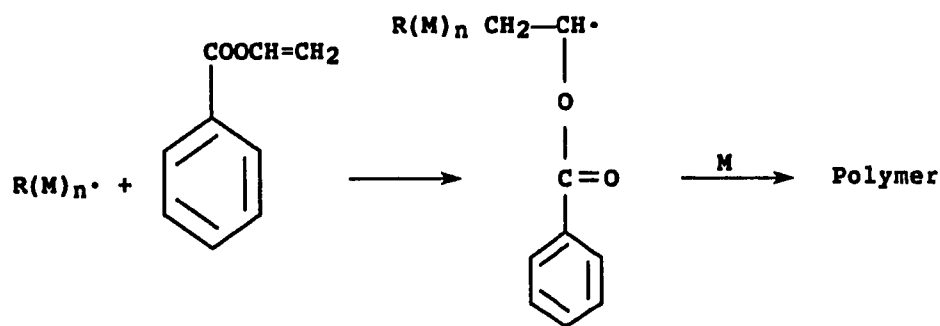
When the mechanism was studied, it was seen that although their structures were similar, vinyl benzoate polymerized very slowly compared to vinyl acetate. The slow conversion was investigated from different angles. The experimental data revealed that part of the slow conversion and the high branching and cross-linking was due to impurities in the monomer.^{22,23} Still the peculiar feature of the vinyl benzoate monomer, which may account for the observed change in degree of polymerization with conversion, is the probable addition of free radicals to the phenyl ring shown in the following scheme.¹⁹



Free radicals can add to the monomer or to the polymer.



Besides the addition to the aromatic nucleus, normal polymerization also proceeds as seen below:



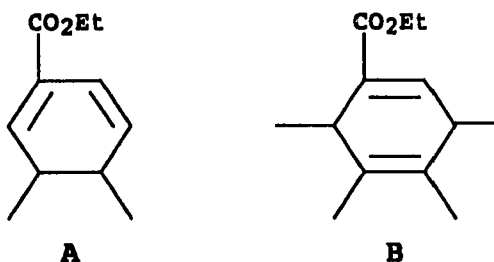
In these and similar reaction equations "M" signifies either a monomer molecule or a unit derived from a monomer within a polymer molecule, depending on where it is used.

The presence of an ester group attached to the phenyl ring renders the hydrogen atom in the ortho and para positions labile and easily removed by a free radical leaving a free radical site on the benzene ring. In solution polymerization, because the concentration of the polymer molecules remains smaller (compared to its value in bulk polymerization) during the initial stages of polymerization, the probability of exchange reaction occurring with polymer molecules is much less. Smets and Hertoghe²⁴ confirmed the existence of branching in the polymer chain when they observed a

significant decrease in molecular weights after the hydrolysis of polymers.

As ring activation seemed to play an important role, copolymerization studies were done with substituted vinyl benzoates. A marked increase in conversion and a decrease in reaction time at higher temperatures obtained with vinyl p-methoxy benzoate, vinyl p-chlorobenzoate, and vinyl o-chlorobenzoate proved the role of activation experimentally.¹⁹

Studies were made to find the extent of copolymerization of aromatic groups.^{22,25} If this really occurs, then the resulting polymer will have structures derived from the phenyl rings within the backbone chain. Santee and coworkers²² obtained ultraviolet spectra of the polymerization product of vinyl acetate and ethyl benzoate which showed that there was one cyclohexadiene group per 500 vinyl acetate groups, in the form of either isomer (A) or (B), from which only (A) could be easily detected by ultraviolet analysis, being a conjugated diene chromophore.



These studies show that even if to a small extent, copolymerization of vinyl monomers with aromatic compounds does take place.

Kamachi et al. in two separate studies^{26,27}, determined the rate constants for radical polymerizations of vinyl benzoate and vinyl acetate in different solvents and reported that although polyvinyl benzoate radical was more reactive than polyvinyl acetate radical, the polymerization rate of vinyl benzoate was lower, most probably because of the formation of an intermolecular complex between the propagating radical and the aromatic ring.

The studies clearly indicate the existence of some kind of a self-inhibiting mechanism even though it has not yet been clearly understood how. This fact encourages research on methods to improve the rate of polymerization.

Emulsion Polymerization

All the studies mentioned above were done using bulk or solution polymerization. There has been no work reported on emulsion polymerization of vinyl benzoate and how it affects conversion and molecular weights. Emulsion polymerization usually enables the synthesis of high molecular weight polymers with very high rates and at the same time eliminates the difficulties in heat dissipation, stirring and handling of end product.

Emulsion polymerization of other monomers has been studied extensively in the past years using a variety of initiator systems and emulsifier systems, which are the two key areas. This present work has concentrated on trying various systems on the emulsion polymerization of vinyl benzoate.

A simple recipe for emulsion polymerization comprises four ingredients, the monomer, the continuous phase (water), the emulsifier and the initiator. To obtain satisfactory polymerization it is necessary to choose the most appropriate ingredients, remove atmospheric oxygen fairly thoroughly by flushing the monomer and gas space with nitrogen, and subject the ingredients to moderate agitation. The special precaution with oxygen is necessary because it can add to double bonds and form peroxides. These peroxides will not only affect the reaction rate but also the quality of the product.

However while the polymerization system is fairly simple, the properties of the product greatly depend on the properties of the emulsifier and initiator. Therefore they deserve extensive study and careful preparation.

Emulsifiers

The emulsifier influences the polymerization rate and properties of the latex, including particle size, particle size distribution and stability, and its choice in practical systems is important. Emulsifiers are classified into anionic, cationic, and non-ionic types but all are characterized by the presence in the molecule of water soluble and water insoluble portions. They form normal solutions in solvents at high dilution but abruptly change into aggregated forms, termed micelles, at specific and usually relatively low concentrations. In aqueous solutions the inner portion of the micelle contains the hydrocarbon or other water

insoluble component of the molecules, while the hydrophilic portion is located at the surface.

The change at the critical micelle concentration occurs so as to minimize the free-energy of the solution and, in general, the molecular weight of the micelle increases as the size of the water insoluble segment increases. In compounds containing linear aliphatic hydrocarbon chains there is little activity below C₁₀, while limited solubility restricts the use of emulsifiers containing alkyl groups greater than C₁₈. Micelle formation is accompanied by changes in the properties of the solution, the best known of which is the abrupt change in the relationship between the surface tension of the solution and the concentration of the emulsifier.

Important anionic emulsifiers are fatty acid soaps and salts of linear and branched chain alkyl hydrogen sulfates and sulfonic acids, alkyl benzene sulfonic acids, and alkyl naphthalene sulfonic acids. The usual counter ions are Na⁺, K⁺, and NH₄⁺.

Cationic surfactants are almost restricted to quarternary ammonium salts with bromide or chloride counter ions. They are not widely used commercially, and they frequently are associated with low rates of polymerization. This arises particularly when the positive charge on the polymer particle is opposite to that of the initiating radicals, for example SO₄⁻.

There are numerous non-ionic emulsifiers of widely differing structure. They are often complex mixtures and may be of high molecular weight. The more important ones contain polyoxyethylene

chains with one end attached to a hydrophobic group and the other end to a hydroxyl group. The onset of micelle formation occurs at weight concentrations comparable to those of the ionic surfactants, but the surface tension reduction is not usually so great. As with the ionic emulsifiers, it is presumed that the water soluble part of the molecule envelops an inner hydrophobic portion, and in some cases, but not all, there is a clear evidence for the formation of micelles. Most of these materials have molecular weights in the range 300-8000, but in principle there is no specific limit, as shown by certain water soluble high polymers such as partly acetylated polyvinylalcohol.

The formation of micelles takes place only in the beginning of the polymerization. The concentration of the free detergent decreases rapidly during the early stages, because of its adsorption on growing polymer particles. The polymer particles solubilize monomers and at this stage the detergent is almost completely adsorbed on the surface of the particles and now functions to protect the particles from flocculation. If flocculation is desired, it can be brought about by destroying the electrical double layer around the particles, usually using large amounts of alcohol or of high ionic strength electrolytes like aluminum sulfate.

There has also been some research in the area of mixed surfactants referring to mixtures of ionic and non-ionic surfactants. With such systems it was experimentally observed²⁸

that there was a decrease in particle size which led to an increase in the rate of polymerization.^{29,30,31,32,33}

Initiators

The most widely used initiators for emulsion polymerizations are water soluble peroxy salts, e.g. ammonium, potassium, and sodium peroxydisulfates, and organic hydroperoxides, such as cumene hydroperoxide. No oil soluble peroxide has been proven to have practical utility as an initiator in emulsion polymerization, in the absence of a reducing agent. Most organic peroxides are soluble in monomer and insoluble in water, which causes difficulties by initiating polymerization in the monomer droplets rather than in swollen micelles.

The advantages of emulsion polymerization stem from the introduction of free radicals, one at a time, into a large number of small isolated micelles. Oil soluble peroxides, in the absence of a reducing agent, form two free radicals at once in a given micelle. Thus, in a very small micelle the two resulting growing chains will terminate each other before they can grow to high molecular weight. Another big disadvantage of oil soluble peroxides is that after the initial stages of the polymerization, they stay dissolved in the monomer droplets and do not go into the micelles.

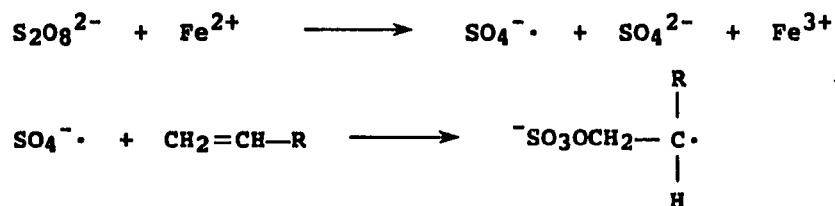
An outstanding development in the field of initiators has been the use of redox systems in which an oxidizing and a reducing agent, each thermally stable by itself, react to form radicals at low or moderate temperatures. Some common oxidizing agents are potassium

peroxydisulfate, potassium hexacyanoferrate(II), potassium permanganate, t-butyl hydroperoxide, and cumene hydroperoxide. A common reducing agent is ferrous sulfate usually used with a second reducing agent such as glucose, fructose, dihydroxy acetone or sodium thiosulfate.

In a redox system, for example a mixture of ferrous sulfate and potassium peroxydisulfate, the radical generation is 100 times faster at 10°C than that of potassium peroxydisulfate alone at 50°C.

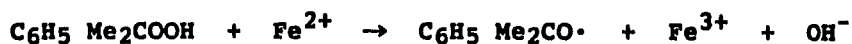
However, there is a tendency with this type of initiator system for rapid and uncontrolled generation of free radicals, which increases greatly with the rise in temperature. When that happens, the polymerization may die out before it is complete, a phenomenon known as "dead end polymerization."

In peroxydisulfate redox systems the sulfate radical ion is formed in the first step shown below, followed by reaction with a monomer molecule:

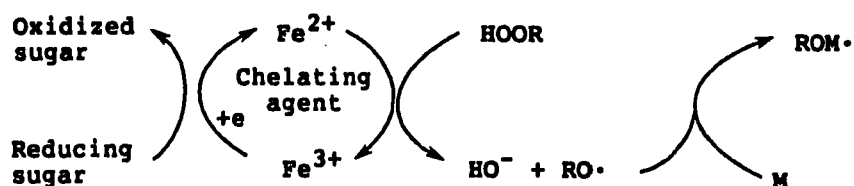


Other redox systems that have been tried include peroxydisulfate-thiosulfate, hexacyanoferrate(III) and pentacyano-nitritoferrate(III) with mercaptans (RSH) to initiate polymerization by production of $\text{RS}\cdot$ radicals. Potassium chromate used with arsenic(III), antimony(III) and tin(II), has also been found to be

an effective redox initiator.¹⁵ Another frequently used system is cumene hydroperoxide and ferrous ion, shown below:



In redox recipes sugars and polyamines have been used as reducing agents. In general any compound containing a carbonyl group and a hydroxyl group on adjacent carbon atoms will function satisfactorily in recipes, for example acetal, dihydroxy acetone, benzoin, galacturonic acid, glucose and fructose. The mechanism by which these initiating systems function is still in doubt, and it is possible that several of the mechanisms which have been proposed may play roles of varying importance at different temperatures.³⁴ A proposed scheme of such an interaction is given below:³⁵



Other Additives

Chain transfer agents are used to control the molecular weight, which is essential in emulsion polymerizations. Chain transfer agents are also useful in cases where the monomer gives rise to undesirable polymer cross-linking. As chain length is shortened, the possibility of extensive branching which leads to cross-linking is minimized. Generally C₈-C₁₆ straight- or branched-chain mercaptans, which are soluble in monomer, are used for this purpose.

Experimental Approach Used in this Study

Vinyl benzoate was synthesized using the vinyl interchange reaction described by Hermann and Haehnel⁶, and Toussaint and Dowell⁷. This method was adopted because of its mild reaction conditions, high yields, quick preparation, low yields of by-products and the simplicity of the apparatus.

To improve the polymerization rate and decrease branching and cross-linking, emulsion polymerization was used, and a number of initiators and emulsifiers were tried in different combinations together with changing temperatures. The method did give high polymerization rates at much shorter reaction times than those previously reported in bulk or solution polymerization.

In addition to studies of optimum conditions for high polymerization rates, viscosity average molecular weights were determined for various combinations and compared to each other.

Also the cohesive energy density, the nuclear magnetic resonance spectrum, the infrared spectrum of the polymer film and the ultraviolet spectrum of polyvinyl benzoate as well as its refractive index increments in two solvents were measured.

CHAPTER II

EXPERIMENTAL PROCEDURE

Materials Used

Different recipes were tried in this work, sometimes by only changing the temperature, initiator or emulsifier. As the same chemicals were used with different combinations and amounts, to avoid repetitions their purification methods and sources are listed in one section.

The following commercial materials were used without further purification. Potassium peroxydisulfate, sodium hydrogen carbonate (reagent grade), and toluene (ACS certified), were from J. T. Baker Company. Sodium thiosulfate, sodium sulfide, iron(II) sulfate, sodium pyrophosphate (crystals) and ethylenediaminetetraacetic acid (reagent grade), were from Mallinckrodt. Caffeine (reagent grade) was from Calbiochem. Potassium dichromate (reagent grade) was from Will Scientific Company. Dihydroxy acetone (98% pure) was from Columbia Company. Cyclopentanone (ACS certified), m-xylene, cumene hydroperoxide (80%), dibenzoyl peroxide (99%), and dodecyl mercaptan (reagent grade), were from Aldrich Chemical Company. Arsenic trioxide (reagent grade) was from Allied Chemical Company. Chloroform (spectrophotometric grade), and methanol (ACS certified) were from Burdick and Jackson Laboratories, Inc. Sodium dodecyl benzenesulfonate (85%) was from Pfaltz and Bauer, Inc. Emulphogene® BC-840 (polyoxyethylated tridecyl alcohol, 100%) was

from GAF Corporation. Sodium hydrogen sulfite, copper(II) sulfate, glucose, fructose, dimethyl aniline, benzoquinone, sodium lauryl sulfate (reagent grade), acetone, methyl ethyl ketone, acetic acid, methyl benzoate, hexane, petroleum ether, ethanol, and ethyl acetate (ACS certified), were from Fisher Scientific Company.

Styrene (reagent grade, Fisher Scientific Company) was distilled under vacuum, over calcium metal. The fraction boiling at 60°C and 45 torr was used in polymerizations.

Vinyl acetate (reagent grade, Aldrich Chemical Company) was distilled at 78°C, with a fractionating column, and the middle fraction, which was 80% of the distillate by volume, was used in polymerizations.

Vinyl benzoate was prepared by the ester exchange reaction between vinyl acetate and benzoic acid, using mercuric acetate as a catalyst. Vinyl acetate was dried over calcium chloride and distilled through a fractionating column. Benzoic acid (61g, 0.50mol) was dissolved in vinyl acetate (277g, 3.22mol) and mercuric acetate (3.66g, 0.0115mol), then 0.5g sulfuric acid was added slowly with stirring. The mixture was refluxed at 80°C for three hours. Any solid residue was filtered using quantitative filter paper (Whatman 42 ashless) and a Buchner funnel with vacuum. The filtrate was then distilled under vacuum. The fraction that boiled between 60 and 65°C at 3 torr was collected and used in polymerizations. Gas chromatography analysis showed only one peak, so this synthesis method was considered to give pure product suitable for

tion reactions. From this point on the purity of vinyl benzoate was checked with refractive index measurements.

Polymerization

General Procedure

The recipes used in this study were variations of the basic recipe shown below:

Component	Parts by Weight
Monomer	100
Water	180
Detergent	5
Initiator	0.2

In some experiments the water was increased to the ratio of 1 part monomer to 3 parts water, by weight.

All the polymerizations were run in three-neck, round-bottom glass flasks. Reaction flasks were kept in a constant temperature bath controlled to $\pm 0.1^{\circ}\text{C}$. The reaction mixtures were stirred with magnetic stirrers.

Before each polymerization, the reaction flask was cleaned with soap and water twice, rinsed with acetone and with distilled water and dried in an oven at 100°C . Then the emulsifier, water, redox chemicals, chain transfer agent, initiator and finally the monomer were placed in the flask, in this order. All ingredients were normally weighed to $\pm 0.001\text{g}$ using a Mettler H-8 balance. In the kinetic experiments the ingredients were weighed to $\pm 0.0001\text{g}$, using a Mettler AE-160 balance. After the charge was completed, a teflon-

coated magnetic stirring bar, cleaned by the same procedure used for the reaction flask, was added to the flask. The flask was then purged for one minute with 99.99% certified grade nitrogen (Union Carbide Corporation). A purge time of one minute was considered sufficient, because the distilled water used in preparing all aqueous solutions, and as the polymerization medium, had been boiled for ten minutes, cooled, purged with nitrogen for several minutes and kept in a tightly stoppered flask.

Samples of the mixture during polymerization were rapidly pipetted out into aluminum boats filled with approximately one gram of Celite® (Johns-Manville Company). During sample taking the flasks were purged with nitrogen to prevent oxygen from entering the flask. The samples taken thus were weighed within ten seconds to minimize the evaporation of the liquid phase. After each sample was weighed, 0.5mL of 1% benzoquinone solution in 95% ethanol was added to the contents of the boat to stop any further polymerization. The samples were then dried at 100°C for three hours. A blank determination was made with just Celite and benzoquinone solution. The amount of moisture or volatile material left after drying was undetectable in weighings to $\pm 0.0001\text{g}$. Three hours is considered to be a suitable drying time. After 2.5 h at 100°C the boats reach constant weight. The weights obtained after oven drying were corrected for the amount of residue besides the polymer.

In the kinetic reactions, samples were taken every 15 min for ten hours, and weighings were made to $\pm 0.0001\text{g}$.

Exploratory Preparations

The amounts of ingredients in recipes, polymerization times and temperatures, and the resulting yield can be seen in the tables in Appendix A.

In the first eight recipes potassium peroxydisulfate is used as an initiator by itself or in redox system. These recipes are given in Table I, Appendix A (A-I), page 82.

The next seven recipes used cumene hydroperoxide either by itself or in redox systems. They are listed in Table A-II, page 83.

In recipes 16 and 17 potassium dichromate was used in redox systems, in 18, air, and in 19 dibenzoylperoxide were used as initiators. These recipes can be seen in Table A-III, page 84.

In recipes 20 to 25, dibenzoylperoxide by itself or in the presence of tertiary amines was used as an initiator, and the results are given in Table A-IV, page 85.

In recipes 26 and 27 styrene and vinyl acetate were polymerized using potassium peroxydisulfate as initiator. These two recipes are given in Table A-V, page 86.

For the polymerizations that were done to study the effect of changing temperature, emulsifier and initiator on the conversion of polyvinyl benzoate, the next twenty recipes were used.

Recipes 28-39 reflected the effect of changing emulsifier concentration and composition on the conversion using potassium peroxydisulfate as initiator. Recipes 28 to 31, given in Table A-VI show the effect of increasing temperature with sodium lauryl sulfate as detergent. Table A-VII has recipes 32 to 35, showing the effect

of increased temperature on a mixture of detergents, using sodium lauryl sulfate as the anionic detergent and emulphogene® BC-840 as the nonionic detergent. Table A-VIII, with recipes 36 to 39, shows the effects of temperature on a recipe containing twice the amount of detergent as was used in the basic recipe.

In recipes 40 to 43, in Table A-IX, the significance of the concentration of sodium hydrogensulfite in polymerizations initiated by potassium peroxydisulfate was studied.

Table A-X shows the results of the studies done with cumene hydroperoxide at different temperatures and increasing emulsifier concentrations, with recipes 44 to 47.

These studies were pursued further by limiting the polymerization conditions to two temperatures, 60° and 75°C, and using different emulsifiers with a higher ratio of water to monomer. In this group of experiments the emulsifier concentration was doubled compared to the basic recipe.

Recipes 48 and 49 in Table A-XI show the effect of increasing temperature. Emulphogene® BC-840, a nonionic detergent was the only emulsifier.

Recipes 50 and 51 show the effect of increasing temperature when dodecyl benzene sulfonate was the only emulsifier. In recipe 52, the effect of added Emulphogene BC-840 as a nonionic detergent to dodecyl benzene sulfonate was studied. Recipes 50 to 52 are shown in Table A-XII.

Recipes 53 to 58 in Table A-XIII, show the effect of increasing the temperature and increasing the amount of water, and the addition of sodium hydrogensulfite as a reducing agent.

Rate Studies

In Table A-XIV are recipes used to study the effects of emulsifier and initiator concentration on the rate of polymerizations. Recipes 59, 60 and 61 were used to determine the effect of emulsifier concentration, and recipes 62, 63, and 64 involved changes of initiator concentration.

In these rate studies samples were taken every 15 min. Recipe 38 was chosen as a basis for these recipes, and the temperature was set to $75.0 \pm 0.1^\circ\text{C}$. Potassium peroxydisulfate, used as the initiator, was dissolved in water, and a calculated amount of the initiator solution was added to each reaction mixture after it had been brought to the reaction temperature with the constant temperature bath. The time of the addition of the initiator was taken as time zero, or the starting time of the polymerization.

Unfortunately from the kinetic study standpoint, but fortunately from a product preparation standpoint, conversions were very high in a very short time. In order to obtain useful kinetic data, the temperature was lowered to $60.0 \pm 0.1^\circ\text{C}$.

In these polymerizations, recipes 65, 66 and 67 were used to show the effect of the changing emulsifier concentration, and recipes 68, 69, and 70 were used to study the effect of changing the

concentration of the initiator. These recipes can be seen in Table A-XV.

Properties of Vinyl Benzoate and its Polymer

Dilute Solution Viscosity

The viscosity average molecular weights of selected polymer samples were determined by dilute solution viscosity measurements using an Ostwald viscometer and an Ubbelohde viscometer in a constant temperature bath maintained at $30.0 \pm 0.1^\circ\text{C}$.

For the solubility studies, polyvinyl benzoate was precipitated by adding the latex to a ten-fold volume of methanol. The precipitate was collected on a filter, redissolved in toluene and reprecipitated in hexane. Other suitable solvents for this purpose are ethyl acetate, chloroform, methyl ethyl ketone and acetone. Suitable nonsolvents are petroleum ether (bp. $30\text{--}60^\circ\text{C}$), methanol, ethanol (95%), 2-propanol and salt water (10% NaCl by weight). Among these possibilities the best solvent/nonsolvent pair for reprecipitation of polyvinyl benzoate was found to be toluene-hexane.

The intrinsic viscosity of each sample of twice-precipitated polyvinyl benzoate was determined using an Ubbelohde viscometer. For each sample five different concentrations, usually 0.75, 1.2, 1.5, 1.875 and 2.0 g/dL were used. For these solutions weighings were done with a precision of $\pm 0.0001\text{g}$ and solutions prepared in ten milliliter volumetric flasks. In these preparations it was

assumed that the volume of solvent would be equal to the volume of the solution because in reality they are very close to each other and when values are extrapolated to zero concentration this small deviation becomes insignificant.

As the utmost cleanliness of the glassware is essential for reproducible results in efflux time measurements in a viscometer, and as it is known that chromic acid cleaning solution changes the characteristics of the glass capillary in viscometers making frequent calibrations necessary, in this study the Ubbelohde viscometer was cleaned with alcoholic concentrated nitric acid. This method should be followed carefully inside a hood with safety glasses. The lower bulb of the viscometer is half filled with concentrated nitric acid. Then two drops of ethanol or 1-propanol is dropped into the viscometer. The reaction proceeds after a one or two minute induction period with the solution turning brown, becoming hot and evolving brown oxide fumes. After the initial reaction subsides two more drops of alcohol are added. This time there is no induction period and an immediate reaction proceeds with extensive foaming accompanied by gas evolution. After the reaction slows down some of this cleaning mixture is forced into the capillary tube and upper bulb with gentle air pressure to assure complete cleaning. The viscometer is emptied after a 10-15 minute cleaning period, rinsed well with distilled water and dried in an oven. In all cleaning and efflux time determinations liquid was forced into the capillary tube by low pressure filtered air to

prevent losses of solvent seen in methods where liquid is drawn into the capillary tube with suction.

For the determinations with the Ostwald viscometer, after thoroughly cleaning the viscometer, first the efflux time for the pure solvent was determined and recorded. Then the viscometer was dried in the oven, the first solution of polyvinyl benzoate was added, the system brought to the water bath temperature for five minutes and the efflux time was determined and recorded for the solution. After each solution the viscometer was rinsed twice with pure solvent and dried in the oven. The efflux time was determined with a Precision Scientific Company chronometer up to ± 0.05 s and the efflux time determination was repeated at least three times, until a reproducibility of 0.1% of the mean value was reached.

For the determinations with the Ubbelohde viscometer, after thoroughly cleaning the viscometer, first the efflux time for the pure solvent was determined and recorded. Then one milliliter of a 0.3g/10mL concentrated polymer solution was added. As this polymer solution was also kept in the constant temperature bath, it was not necessary to wait for the temperature of the solution to reach the water bath temperature. The solution in the Ubbelohde viscometer was then thoroughly mixed by running it up the viscometer ten times. The efflux time was determined with a Precision Scientific Company chronometer up to ± 0.05 s and the efflux time determination was repeated at least three times, until a reproducibility of 0.1% of the mean value was reached. After the completion of each efflux

time determination another milliliter of concentrated solution was added and the procedure was repeated.

The experimental data and graphs used to obtain intrinsic viscosities used in molecular weight determinations can be seen in Appendix B, page 93. The experimental data and graphs used to obtain intrinsic viscosities for estimation of cohesive energy density are given in Appendix C, page 99.

Spectra

The proton nuclear magnetic resonance spectrum of both the monomer and polymer were obtained using an IBM Model AF-200, 200 MHz Fourier transform NMR spectrometer, with deuterated chloroform as the solvent.

The ultraviolet spectrum of 0.16mg/mL polyvinyl benzoate solution in chloroform was obtained using a Hewlett Packard Model 8451 A Diode Array Spectrophotometer, over a range of 200nm to 300nm.

For the infrared spectra the Beckman Acculab 8 instrument was used. The spectrum of the monomer was obtained, neat, with rock salt plates.

For the IR spectrum of the polymer a film was made by adding a concentrated acetone solution of the polymer, purified by reprecipitation, drop by drop onto the surface of distilled water in a petri dish. As the acetone quickly dissolves in water (and some evaporates), a thin film of polymer is formed on the surface of the water. This polymer film is then thickened by successive drops of solution. After the film comes to a thickness where it will not

break easily, it was lifted onto a watch glass with the aid of a spatula and dried there for three days at room temperature. The dried film then was cut and taped onto a piece of cardboard which was precut to the size of the solid sample holder plate of the IR spectrophotometer, with a hole cut out for transmittance.

Usually the polymer films for infrared samples were made by the solution casting method. In this method the polymer was dissolved in a suitable solvent to make a viscous solution. Then the solution was poured onto a flat, nonadhesive solid surface, and the solvent was allowed to evaporate. Once the film was dry it could be peeled from the flat surface.

Another variation of the solution casting method is to pour the viscous polymer solution onto the surface of mercury in a suitable container. The container is placed in a vibration free area until the solvent evaporates. The film is then removed and the thicker circumference, due to the meniscus of the mercury, is cut off.

However both these methods gave unsatisfactory results in this study. The mercury method gave an extremely fragile film that could not be lifted from the surface of the mercury in a large enough piece. Casting attempts on a flat surface failed because the film was not strong enough to be lifted.

Refractive Index Increment

For the determination of refractive index increments a Brice-Phoenix model BP-2000-V differential refractometer was used. Solutions in methyl ethyl ketone and ethyl acetate were prepared by

dissolving $0.01 \pm 0.0001\text{g}$ of polymer in $10.0 \pm 0.0001\text{g}$ of solvent. The concentrations were reported in g/mL of solvent by converting grams of solvent into volume with the aid of temperature-density graphs.³⁶

In the present work the mercury green line (546nm), and the relationship, $\Delta n = 0.9144 \times 10^{-4} \Delta d$, of the calibrated⁴¹ instrument was used.

CHAPTER III

RESULTS AND DISCUSSION

Emulsion Polymerization of Vinyl Benzoate

The purpose of this study is to find a polymerization method for vinyl benzoate that will give a higher rate, higher molecular weight and lower branching than the ones studied so far. In previous polymerization studies, in bulk and in solution, low molecular weight polymers with troublesome crosslinking were reported.

To solve these problems, emulsion polymerization was thought to be a suitable method. This method normally gives high rates and molecular weights. The polymerization to a large extent happens in micelles that are separated from each other by water. Therefore terminations with binary collisions or, as will be explained later, the ring participation in free radical additions are minimized. Thus it might be possible to increase the reaction rate together with the molecular weight and decrease the crosslinking. As the emulsion polymerization of vinyl benzoate had not been studied, this method was chosen as the basis of the present study.

The vinyl interchange reaction was used for the laboratory synthesis of vinyl benzoate. This method has very mild reaction conditions and short reaction times of about three hours. Yields are about 75%. The product is chromatographically pure (by gas chromatography), and its refractive index is in good agreement with literature values.

One of the advantages of emulsion polymerization is that it has three main variables, initiator concentration and type, emulsifier concentration and type, and temperature that can be manipulated to find a suitable combination for desired goals. Although these possibilities introduce a lot of complications, some of which still are not fully understood, they also provide possibilities for improvements. For instance, redox systems generate radicals much faster than simple free radical generators and thus permit polymerizations to be run at much lower temperatures. Mixed anionic and nonionic surfactants sometimes result in higher rates of polymerization, or a particular emulsifier may work much better than others with a particular monomer-initiator system.

As stated earlier, the benzene ring in vinyl benzoate has been thought to participate in free radical polymerizations by reacting with a free radical.¹⁷ If chain lengths are shortened, most probably crosslinking will be reduced. Therefore, it was thought that a chain transfer agent serving this purpose might bring a significant improvement to this problem.

The following groups of studies were done with the hope of testing this theory and of reaching high conversions in relatively short times.

Initiator Systems

The first group of studies were done with different free radical initiators. These results were compared with redox systems using the same initiators.

First potassium peroxydisulfate was used by itself or in redox systems. These results are summarized in Table 1.

TABLE 1
Emulsion Polymerization of Vinyl Benzoate Using Potassium Peroxydisulfate as an Initiator

Recipe Number	Initiator	K ₂ S ₂ O ₈ ^b %	Temperature °C	Time h	Conversion %
1	K ₂ S ₂ O ₈	0.20	50	20	26
2	K ₂ S ₂ O ₈	0.20	71	12	35
3	K ₂ S ₂ O ₈	0.20	45	18	57
4	K ₂ S ₂ O ₈ , NaHSO ₃ ^c	0.16	50	18	18
5	K ₂ S ₂ O ₈ , NaHSO ₃ , glucose, FeSO ₄	0.25	60	12	38
6 ^a	K ₂ S ₂ O ₈ , NaHSO ₃ , glucose, FeSO ₄	0.25	0	18	8
7	K ₂ S ₂ O ₈ , NaHSO ₃ , glucose, FeSO ₄	0.25	0	23	4
8	K ₂ S ₂ O ₈ , Na ₂ S ₂ O ₃ , CuSO ₄	0.09	0	20	6

^a The emulsifier in recipe 6 was a mixture of sodium lauryl sulfate and Emulphogene BC-840. In all other recipes, sodium lauryl sulfate was used alone.

^b The concentration of initiator is based on monomer amount.

^c For the concentrations of components other than potassium peroxydisulfate, see tables in Appendix A.

In all redox recipes, 4, 5, 6, 7, and 8 conversions were very low. Although redox initiator systems usually yield much higher conversions at lower temperatures, recipes 6, 7, and 8 gave even lower yields in this study.

The following experiments with cumene hydroperoxide (CHP) and some other redox systems were studied to see if the same pattern existed. The anionic emulsifier sodium lauryl sulfate is abbreviated as SLS and the non-ionic emulsifier Emulphogene BC-840 as E. Table 2 has results from cumene hydroperoxide and Table 3 from other redox systems.

TABLE 2
Emulsion Polymerization of Vinyl Benzoate Using
Cumene Hydroperoxide as an Initiator

Recipe Number	Initiator	CHP ^a %	Emulsifier	Temp. °C	Time h	Conversion %
9	CHP	0.50	SLS & E	50	19	27
10	CHP, FeSO ₄ , glucose	0.10	SLS	0	12	8
11	CHP, FeSO ₄ , glucose	0.10	SLS	0	18	9
12	CHP	0.17	SLS	0	23	8
13	CHP, FeSO ₄ , dihydroxy acetone	0.05	SLS & E	0	20	7
14	CHP, FeSO ₄ , fructose, Na ₂ S·9H ₂ O	0.17	SLS & E	36	19	17
15	CHP, FeSO ₄ , Na ₂ S·9H ₂ O	0.17	SLS & E	0	19	5

^a Concentrations of all components besides CHP are listed in Appendix A.

The results of the cumene hydroperoxide experiments in Table 2 strengthened the idea that these particular redox systems gave low conversion for the polymerization of vinyl benzoate at low temperatures. The same effect can be seen in recipes 16, 17 and 18

in Table 3, where conversions with redox systems are low even at higher temperatures.

TABLE 3
Emulsion Polymerization of Vinyl Benzoate Using
Various Initiator Systems

Recipe Number	Initiator	Initiator ^a %	Emulsi- fier	Temp. °C	Time h	Conversion %
16	K ₂ Cr ₂ O ₇ , As ₂ O ₃ , FeSO ₄	0.30	SLS & E	56	20	6
17	K ₂ Cr ₂ O ₇ , As ₂ O ₃	0.30	SLS & E	56	19	8
18	Air, FeSO ₄	—	SLS	50	19	9
19	Benzoyl peroxide, FeSO ₄ , fructose	0.09	SLS & E	50	19	7
20	Benzoyl peroxide	0.29	SLS	60	11	28
21	Benzoyl peroxide	0.51	SLS	60	11	16
22	Benzoyl peroxide, N,N ¹ -dimethyl aniline	0.47	SLS	60	10	4
23 ^b	Benzoyl peroxide, N,N ¹ -dimethyl aniline	0.47	SLS	60	10	3
24	Benzoyl peroxide, caffeine	0.47	SLS	60	10	2.5
25 ^c	Benzoyl peroxide, caffeine	0.47	SLS & E	60	10	15

^a Concentrations of all components besides CHP are listed in Appendix A.

^b Recipe 23 has 50% less N,N¹-dimethyl aniline than recipe 22.

^c Recipe 25 has 50% less caffeine than recipe 24.

Studies with redox initiator systems show that higher conversions were obtained if iron(II) sulfate was chelated by sodium pyrophosphate or ethylenediaminetetraacetic acid before it was added to the polymerization charge.³⁵ Unfortunately even this step did not help the low yields of polyvinyl benzoate polymerized with redox initiator systems.

In Table 3 there are also some studies with benzoyl peroxide. Benzoyl peroxide is an oil soluble initiator. Emulsion polymerization on the other hand requires water soluble initiators which produce free radicals that diffuse into micelles and initiate polymerization. Oil soluble initiators have the tendency to diffuse into the micelle than produce free radicals which are immediately terminated by each other. However, there was a remote possibility that, by using tertiary amines which decompose benzoyl peroxide at a higher rate, interesting results could be obtained. Unfortunately this was not the case and all these recipes gave low yields.

After obtaining low yields with low temperature redox polymerization, the focus on this study was shifted to higher temperature polymerizations. The effects of changing temperature, initiator concentration, and emulsifier concentration and type were studied. The outcome of these experiments can be seen in Tables 4, 5 and 6.

In Table 4 only potassium peroxydisulfate was used as an initiator. In recipes 28, 29, 30 and 31 the polymerization temperature was increased and the polymerization rates also

TABLE 4
The Effect of Changing Temperature, Emulsifier Type and Concentration on the Emulsion Polymerization of Vinyl Benzoate

Recipe ^a Number	Emulsifier	Emulsifier ^b %	Temp. °C	Time h	Conversion %
28	SLS	2.8	50	21	20
29	SLS	2.7	60	21	84
30	SLS	2.8	70	12	74
31	SLS	2.8	80	12	90
32	SLS & E	3.0	50	21	33
33	SLS & E	3.0	60	21	88
34	SLS & E	3.0	70	12	83
35	SLS & E	3.0	80	12	94
36	SLS & E	8.2	50	21	87
37	SLS & E	8.3	60	21	90
38	SLS & E	8.3	70	12	89
39	SLS & E	8.3	80	12	90

^a Potassium peroxydisulfate was used as an initiator in all recipes with a concentration of 0.25% based on monomer amount.

^b Emulsifier concentrations are based upon amount of water.

increased. In recipes 32, 33, 34 and 35 a nonionic emulsifier was mixed with an anionic emulsifier and the conversion increased compared to the recipes where only anionic emulsifiers were used. Also rates increased with increasing temperature. In recipes 36, 37, 38 and 39 the amount of mixed emulsifier was doubled and this again had a positive effect in increasing the conversion, especially

at lower temperatures. As expected the yields in this set also increased with increasing temperature. Therefore, it was concluded that in the emulsion polymerization of vinyl benzoate, higher temperatures, higher emulsifier concentrations and mixed emulsifiers were advantageous.

TABLE 5

The Effect of Increasing Sodium Hydrogen Sulfite Concentration, on the Conversion in the Emulsion Polymerization of Vinyl Benzoate^b

Recipe Number	NaHSO ₃ ^a %	Conversion %
40	0.25	38
41	0.17	39
42	0.40	34
43	0.90	51

^a Sodium hydrogen sulfite concentration is based on monomer amount.

^b Reaction temperatures were 50°C; reactions times were 21 hours; initiator was potassium peroxydisulfate and in all reaction was 0.25% of the monomer amount.

In Table 5 the effect of increasing sodium hydrogen sulfite concentration was studied in the redox emulsion polymerization of vinyl benzoate using potassium peroxydisulfate as catalyst. Temperatures and potassium peroxydisulfate concentration were kept constant. There were no significant changes with the increasing sodium hydrogen sulfite concentration.

In Table 6, where cumene hydroperoxide was used as an initiator, the same results were observed as in studies with potassium

TABLE 6
The Effect of Changing Temperature and Emulsifier Concentration
on the Emulsion Polymerization of Vinyl Benzoate^b

Recipe Number	Emulsifier ^a %	Temperature °C	Conversion %
44	3.5	60	4
45	3.5	80	88
46	7.7	60	12
47	7.0	80	74

^a Emulsifier (60% SLS + 40% E) concentration is based upon the water amount.

^b Initiator was cumene hydroperoxide, 0.5% based on monomer amount; reaction times were 21 hours.

peroxydisulfate. Increasing temperature and emulsifier concentration increased the yield. Cumene hydroperoxide generates free radicals at higher temperatures than potassium peroxydisulfate, therefore only two higher temperatures were studied in this group.

Emulsifier Systems

The emulsifier type is very important in emulsion polymerization. Therefore, several polymerizations were done to examine the effects of changing the emulsifier concentration and type on the polymerization of vinyl benzoate. The results are shown in Tables 7 and 8.

In this group of studies it can be seen that mixed anionic and nonionic emulsifiers gave the highest rates, and the nonionics alone gave the lowest, at every temperature. This is consistent with other studies¹⁷ where nonionic emulsifiers also gave low yields.

TABLE 7
The Effect of Temperature and Emulsifier Type
on the Emulsion Polymerization of Vinyl Benzoate
When Potassium Peroxydisulfate is Used as an Initiator

Recipe Number	Emulsifier	Emulsifier ^a %	Mass Ratio, monomer:water	Temp. °C	Conv. %
48	Emulphogene BC-840	5.9	1:2	60	37
49	Emulphogene BC-840	5.7	1:2	75	50
50	Dodecyl benzene sulfonate	5.7	1:2	60	51
51	Dodecyl benzene sulfonate	5.7	1:2	75	91
53	SLS (60%w) + E (40% w)	3.3	1:3	60	80
54	SLS (60%w) + E (40% w)	3.3	1:3	75	89

In all these recipes, reaction times were 21 hours.

^a Emulsifier concentration is based upon the water amount.

Dodecyl benzene sulfonate was less effective than sodium lauryl sulfate according to the above results.

Using potassium peroxydisulfate with sodium hydrogen sulfite had a slight advantage compared to potassium peroxydisulfate alone. Whether this finding will be useful in industrial applications or not can be determined with further studies.

Increasing the water amount compared to the monomer amount helped to stabilize the latexes after the polymerizations were terminated. Also it eliminated many stirring problems seen

TABLE 8

The Effect of Temperature and Emulsifier Type on the Emulsion Polymerization of Vinyl Benzoate When Potassium Peroxydisulfate and Sodium Hydrogen Sulfite are Used as an Initiator System

Recipe Number	Emulsifier	Emulsifier %	Mass Ratio, monomer:water	Temp. °C	Time h	Conv. %
52	Dodecyl benzene sulfonate (60%)+ E (40%)	8.0	1:2	60	3	5
					8	31
					21	57
55	SLS (60%) + E (40%)	7.2	1:2	60	3	8
					8	84
					21	90
56	SLS (60%) + E (40%)	7.4	1:2	75	3	51
					8	73
					21	85
57	SLS (60%) + E (40%)	4.4	1:3	60	3	6
					8	87
					21	89
58	SLS (60%) + E (40%)	4.7	1:3	75	3	44
					8	87
					21	90

previously with low monomer-water ratios, where polymer collected on the stirrer. However, in large-scale polymerizations a strong mechanical stirrer can be used instead of the magnetic stirrers used in this study. This way the need to increase the volume of the equipment can be eliminated.

Rate Studies

There are three stages that have to be considered in the rate studies of emulsion polymerization.

In the first stage, the initiator, that is in the water phase, produces radicals that diffuse into the micelles and initiate polymerizations. It takes time for all the micelles to receive free radicals.¹⁷ At this stage the number of free radicals that are generated per milliliter are much less than the number of micelles, usually by a factor of about 10^5 .

Once all the micelles contain propagating radicals, and no new polymerizing particles are initiated, a steady state is rapidly reached. During this stage there is a balance between the polymer and the monomer in the growing polymer particle. This balance differs from one monomer to another depending on the characteristics of the monomer. At this time the growing polymer particles are stabilized with the surfactant molecules adsorbed onto their outer surface. In the second stage the rate of monomer depletion is constant. The polymer to monomer ratio is kept constant by diffusion of monomer molecules from the large monomer reservoir droplets into the water phase, and from there into the micelle. Monomer concentration in the water phase is kept at a saturation level by diffusion from the monomer droplets or reservoirs.

The third stage occurs after the monomer droplets disappear. The remaining supply of monomer is very small, and the polymerization rate quickly drops as the monomer in the swollen polymer particles is rapidly consumed.

Thus the rate of polymerization can be written as

$$R_p = k_p [M] [P\cdot] \quad (1)$$

where k_p is the propagation rate constant, $[M]$ is the concentration of the monomer in moles/liters and $[P\cdot]$ is the concentration of active particles in moles/liters. R_p is then expressed in units of moles/liter-second.

$[P\cdot]$ can be expressed by

$$[P\cdot] = \frac{10^3 N \bar{n}}{N_A}, \quad (2)$$

where N is number of particles per milliliter, \bar{n} is the average number of radicals per polymer particle and N_A is the Avogadro number. The factor $10^3/N_A$ expresses $[P\cdot]$ in moles/liters. Usually \bar{n} is expected to be 0.5. If the particle size is very large then \bar{n} may be closer to unity and if there is a high desorption of radicals from the polymer particle then \bar{n} will fall below 0.5. Monomers, like vinyl acetate and vinyl chloride, with much degradative chain transfer to monomer, will also show values of \bar{n} less than 0.5.

The combination of equations 1 and 2 yields the expression for polymerization rate as

$$R_p = \frac{k_p [M] \cdot 10^3 \cdot N \cdot \bar{n}}{N_A} \quad (3)$$

In this section of experiments, the effects of increasing emulsifier and initiator concentrations on polymerization rates were studied separately. Recipe 38 was chosen for a starting point. Then the initiator and emulsifier concentrations were increased and decreased. At first the polymerizations were run at 75°C. The results of these experiments, where conversions were carefully

followed by taking samples every fifteen minutes, can be seen in Figures 1 and 2.

In these experiments, in a very short time, very high conversions were obtained at this temperature. It was very difficult to arrive at reliable conclusions under these situations. Therefore to decrease the rate of the reaction these experiments were repeated at 60°C, a temperature where results could be monitored with higher precision. The conversion curves obtained at 60°C can be seen in Figures 3 and 4.

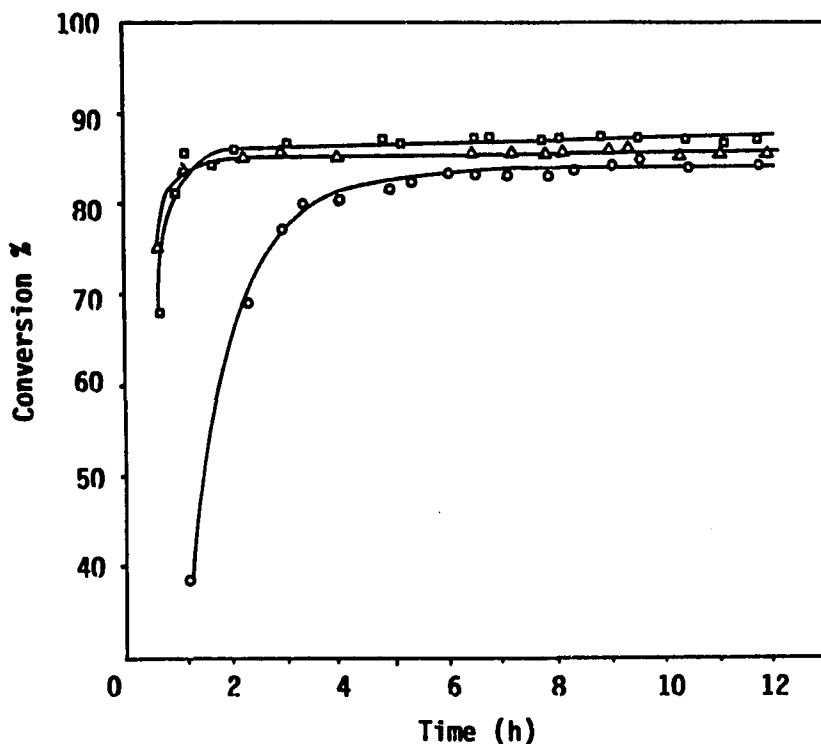


Figure 1. The Effect of Changing Initiator Concentration at 75°

o Recipe 62, initiator, $K_2S_2O_8$, 1.25%

Δ Recipe 63, initiator, $K_2S_2O_8$, 2.5%

\square Recipe 64, initiator, $K_2S_2O_8$, 4.7%

Initiator concentrations are based on monomer amount.

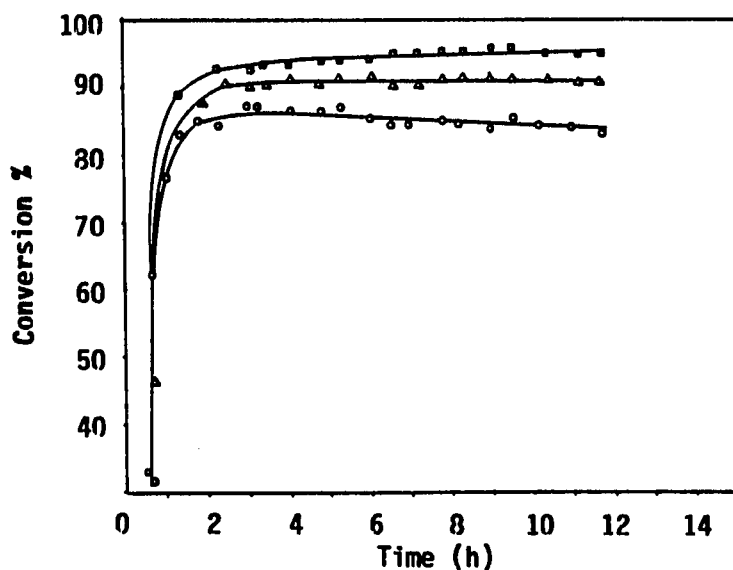


Figure 2. The Effect of Changing Emulsifier Concentration at 75°

Δ Recipe 59, emulsifier, SLS, 1.7%

○ Recipe 60, emulsifier, SLS, 3.5%

□ Recipe 61, emulsifier, SLS, 6.7%

Emulsifier concentrations are based on the amount of water.

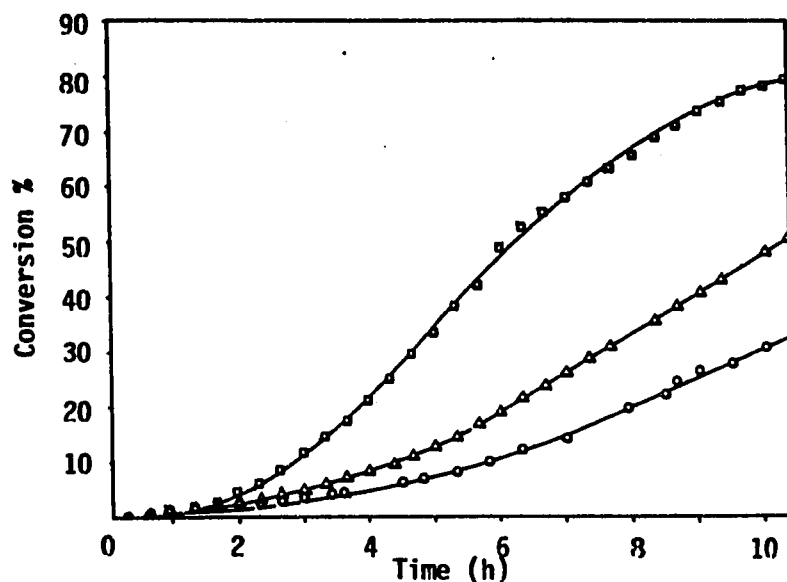


Figure 3. The Effect of Changing Initiator Concentration at 60°

Δ Recipe 68, initiator, K₂S₂O₈, 1.25%

○ Recipe 69, initiator, K₂S₂O₈, 2.5%

□ Recipe 70, initiator, K₂S₂O₈, 4.7%

Initiator concentrations are based upon monomer amount.

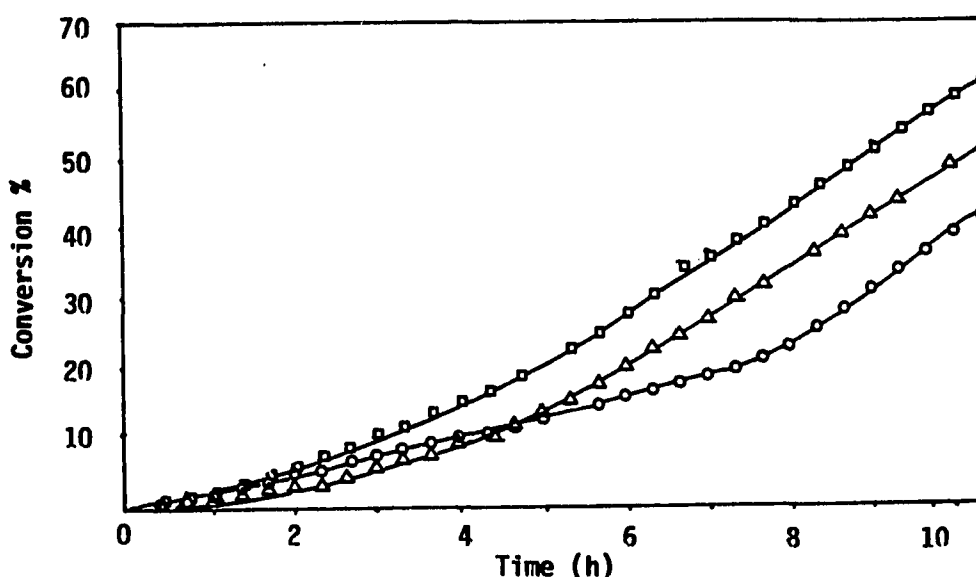


Figure 4. The Effect of Changing Emulsifier Concentration at 60°

△ Recipe 65, emulsifier, SLS, 1.6%

○ Recipe 66, emulsifier, SLS, 3.4%

□ Recipe 67, emulsifier, SLS, 6.7%

Emulsifier concentrations are based on the amount of water.

Each curve in Figures 1, 2, 3 and 4 is the average of two or more polymerizations carried out under identical conditions. Plots of each of the individual curves can be seen in Appendix D.

In emulsion polymerizations, before a steady state is reached, there will still be micelles without free radicals. At this point the rate of initiation, R_i , will be important. The polymer particle number, N , is related to the R_i and the emulsifier concentration, and is derived as,¹⁷

$$N = k \cdot \left(\frac{R_i}{\mu} \right)^{2/5} \left(a_s S \right)^{3/5} \quad (4)$$

In this equation μ is the rate of volume increase of a polymer particle, k is a constant related to the efficiency of radical

capture by the polymer particles, a_s is the interfacial surface area occupied by one emulsifier molecule and S is the total concentration of emulsifier in the system including that in micelles, in solution and on monomer droplets. Thus in the first stage, increasing the emulsifier concentration and initiator concentration is expected to increase the rate. The rate studies of polyvinyl benzoate, as expected, showed higher conversion with increasing initiator and increasing emulsifier concentrations. In this study an increase in the rate of the polymerization of vinyl benzoate was obtained with increasing initiator concentration. However, increasing emulsifier concentrations did not seem to effect the rate. These results can be seen in Figures 3 and 4.

From the combination of the above equations 3 and 4 the below equation can be obtained.

$$R_p = k [R_i]^{2/5} \cdot [S]^{3/5} \cdot [M] \quad (5)$$

A plot of the logarithm of rate versus the logarithm of initiator concentration should give a line with a slope of $2/5$, and a plot of the logarithm of rate versus the logarithm of emulsifier concentration should give a line with a slope of $3/5$.

In the case of vinyl benzoate, the rate did not change with the increasing emulsifier concentration as seen in the slopes of conversion versus time curves of recipes 65, 66 and 67 in Figure 4.

A rate increase was obtained with the increasing initiator concentration seen in the slopes of conversion versus time curves of recipes 68, 69 and 70 in Figure 3. However, the slope of the line

obtained from the plot of logarithm of rate versus logarithm of initiator concentration gave a slope of about one instead of the expected $2/5$ in the above equation. However, there is an uncertainty in the determination of the slopes of the curves. This fact brings an uncertainty to the comparisons of rate of increasing emulsifier and initiator concentration experiments. Therefore a more detailed rate study is necessary to come to a more definite conclusion.

Properties of Polyvinyl Benzoate

Molecular Weight

Viscosity average molecular weights were determined by the Mark-Houwink equation,

$$[\eta] = KM^a \quad (6)$$

where $[\eta]$ is the intrinsic viscosity of the polymer solution, K is a proportionality constant, characteristic of the polymer and solvent, and exponent a is a function of the shape of the polymer coil in a solution, which also is characteristic of the polymer and solvent.

Viscosity measurements were made in an Ubbelohde capillary viscometer. For a given viscometer if t and t_0 are the flow times of the polymer solution and the solvent respectively and ρ and ρ_0 are their densities, the following relationship exists between viscosities ($[\eta]$ for solution and η_0 for solvent) to the first approximation.

$$\frac{\eta}{\eta_0} = \frac{\rho \cdot t}{\rho_0 \cdot t_0} \quad (7)$$

As very dilute polymer solutions are used it can be safely assumed that $\rho = \rho_0$, at least when extrapolated to infinite dilution. Therefore the relationship utilized is

$$\frac{\eta}{\eta_0} = \frac{t}{t_0} \quad (8)$$

The viscosity of the polymer solution divided by the viscosity of the pure solvent is known as the relative viscosity, η_{rel} . The value $\eta_{rel}-1$ is called the specific viscosity, η_{sp} . Specific viscosity divided by the concentration of the solution is known as the reduced specific viscosity, η_{red} , which is related to the intrinsic viscosity, $[\eta]$ by a virial equation shown below

$$\frac{\eta_{sp}}{C} = [\eta] + k_1 [\eta]^2 C + k_1^1 [\eta]^3 C^2 + - - - \quad (9)$$

Intrinsic viscosity, $[\eta]$, is defined as the limit of the reduced specific viscosity as the concentration approaches zero,

$$[\eta] = \lim_{C \rightarrow 0} \left(\frac{\eta_{sp}}{C} \right) \quad (10)$$

For most systems equation 9 can be truncated to the Huggins viscosity relationship shown in equation 11.

$$\frac{\eta_{sp}}{C} = [\eta] + k_1 [\eta]^2 C \quad (11)$$

Intrinsic viscosity can also be found from inherent viscosity, which is the natural logarithm of the relative viscosity divided by the concentration of the polymer solution. The relationship between relative viscosity and intrinsic viscosity is shown in equation 12.

$$\frac{\ln \eta_{rel}}{C} = [\eta] - k_2[\eta]^2 C \quad (12)$$

Extrapolation of the plot of η_{sp}/C versus C or $\ln \eta_{rel}/C$ versus C gives $[\eta]$ as the intercept, as seen in Figure 5. Both lines should intersect the zero-concentration axis at the same point within experimental error. Sometimes there is a slight deviation due to experimental error and the value of the intrinsic viscosity is taken to be the average of the two intersection point values.

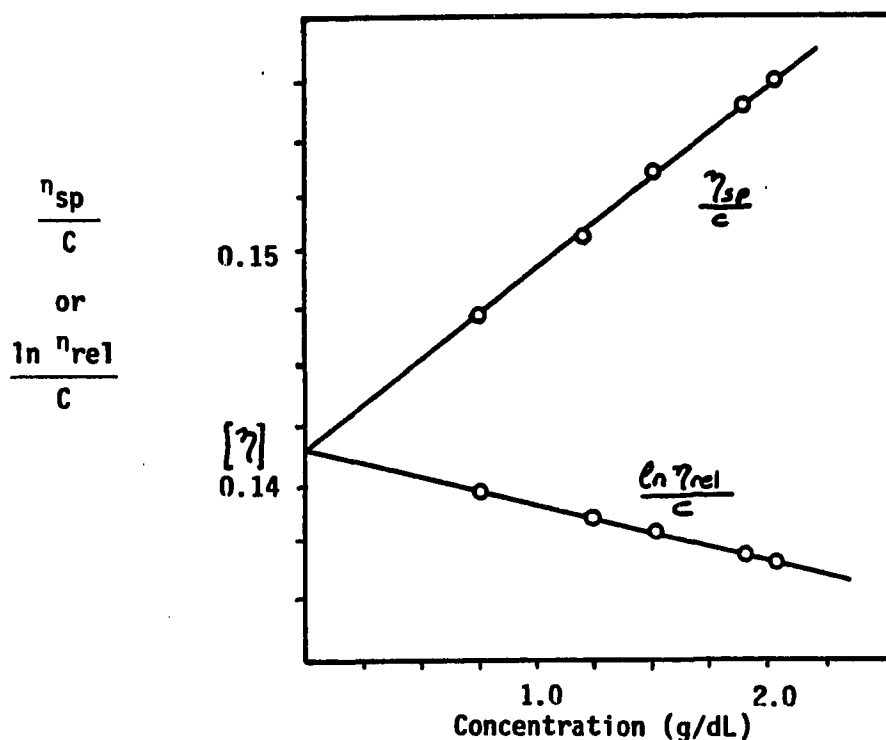


Figure 5. The Intrinsic Viscosity Determination of Polyvinyl Benzoate from Recipe 65 at 32.5°C in Acetone.

The values of k_1 and k_2 can be found from the slopes of these plots. While k_1 and k_2 are mathematically expected to be related by

$$k_1 + k_2 = 0.5,$$

many systems appear not to follow this relationship. This is the case with some samples in Table 9.

There is an important factor in intrinsic viscosity determinations. Erratic behavior in the slopes of the lines of η_{sp}/C versus concentration and $\ln \eta_{rel}/C$ versus concentration is observed if relative viscosity values are less than 1.1 or more than 1.9.³⁸ This strange behavior was also observed in this study. In a series of intrinsic viscosity determinations, low concentrations coupled with low molecular weights of these polymers, gave relative viscosity values that were less than 1.1. Although the precision of the data points were good, the resulting intrinsic viscosity values showed abnormal changes for even a two degree change in temperature. The k_1 and k_2 values were also very far from what is normally observed with polymers. Actually they were so far off that a considerable time was spent on the investigation and the correction of these abnormal numbers. After the calculation methods and the experimental procedure was carefully screened, it was concluded that low η_{rel} could be the problem. There is no scientific explanation, currently, for this behavior. However when these experiments were repeated at higher concentrations, consistent intrinsic viscosity values with changing temperatures, and agreeable k_1 and k_2 values were obtained. Figure 6 illustrates this strange behavior where the

TABLE 9
Molecular Weights of Selected Polyvinyl Benzoate Samples

Recipe Number	$[\eta]$ dL/g	k_1	k_2	k_1+k_2	Molecular Weight	Degree of Polymerization
65	0.1156	0.54	0.0083	0.55	46000	310
66	0.0911	1.60	-0.8000	0.80	35000	230
67	0.0932	0.65	-0.0700	0.58	36000	240
68	0.0994	0.67	-0.0900	0.58	38000	260
69	0.0911	1.60	-0.8000	0.80	35000	230
70	0.0975	0.80	-0.2000	0.60	37000	250
51	0.1507	0.56	0.0040	0.56	63000	420
54	0.1478	0.70	-0.1000	0.60	61000	410
20	0.1130	0.57	-0.0500	0.52	45000	300
Vinyl acetate	0.3980	0.31	0.0600	0.38	98000	1100

intrinsic viscosity of one polymer was obtained at two different sets of concentrations, at one temperature.

In this study methyl ethyl ketone was used as a solvent for intrinsic viscosity determinations at $30.0 \pm 0.1^\circ\text{C}$. The value used for K was 0.126×10^{-4} g/dL and for a was 0.85.³⁷ The molecular weights obtained from the Mark-Houwink equation and the corresponding degrees of polymerization are given in Table 9.

In the first group of recipes 65, 66 and 67, emulsifier concentration was increased and in the second group, 68, 69, 70, the initiator concentration was increased. However there was no correlation between molecular weights and increasing emulsifier concentrations or increasing initiator concentrations in recipes, and molecular weights were generally low. Even vinyl acetate, which

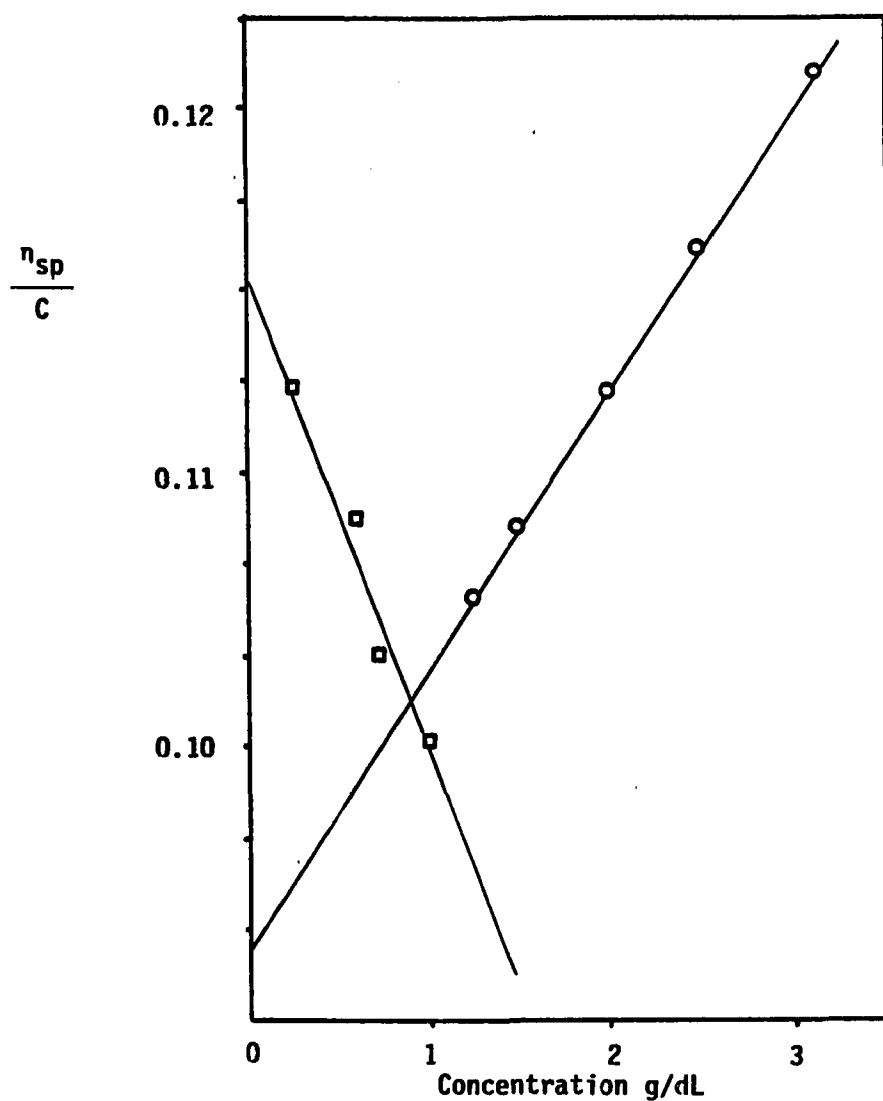


Figure 6. The Change in the Slope of η_{sp}/c vs C with Changing η_{rel} Values, at 30°C, for Polyvinyl Benzoate Obtained from Recipe 70.

- Represents a line when solution concentrations gave $\eta_{rel} < 1.1$.
- Represents a line when solution concentrations gave $\eta_{rel} > 1.1$.

under emulsion polymerization conditions normally gives much higher molecular weights, had a rather low molecular weight. This effect most probably was due to the presence of dodecyl mercaptan, used as a chain transfer agent. It was added to decrease the chain length in hopes of decreasing crosslinking. However at this point, there is no evidence that if the amount of chain transfer agent was decreased to increase molecular weights, crosslinking would also increase. Therefore there is still a possibility of increasing molecular weights without changing the characteristics of the polymer to a great extent.

Cohesive Energy Density

Cohesive energy density, (CED), is a property that plays an important role in determining the solubility of polymers. In a good solvent the adhesive forces between the solvent and the polymer are similar to the cohesive forces that exist between solvent molecules or between polymer molecules. In such a case an exchange of a solvent molecule by a polymer structural unit can occur with little or no change in the interaction forces that exist between solvent or polymer molecules. The strength of the intermolecular forces is represented by the cohesive energy density, which is the molar energy of vaporization per unit volume, $\Delta E/V$.³⁹ The energy of vaporization is ΔE and the molar volume is V , and cohesive energy density has units of cal/cc.

For a solution to take place the free energy, G , must decrease. Therefore in equation $\Delta G_m = \Delta H_m - T\Delta S_m$, the Gibbs free energy change, must be zero or negative. In this equation ΔH_m is the change in enthalpy, ΔS , the change in entropy, T , the absolute temperature and the subscripts, m , represent mixing. For large molecules like polymers change in entropy during solution is small. Therefore at a constant temperature the change of enthalpy becomes important. The enthalpy change is related to the cohesive energy density with the Hildebrand equation (equation 13).

$$\Delta H_m = \phi_1 \phi_2 (\delta_1 - \delta_2)^2 \quad (13)$$

In this equation ϕ_1 is the partial volume of the solvent and ϕ_2 the solute, δ_1 is the solubility parameter of the solvent and δ_2 , the solubility parameter of the solute. The solubility parameter is related to the cohesive energy density as in equation 14, and has units of $(\text{cal/cc})^{1/2}$

$$\delta = \left(\frac{\Delta E}{V} \right)^{1/2} \quad (14)$$

As the solubility parameter values become closer to each other, the enthalpy of mixing becomes very small, the Gibbs free energy of mixing decreases, and the solution process becomes more favored.

Thus, if the δ value for a given polymer is known, by consulting solubility parameter tables of potential solvents, it will be simple to find possible solvents for that polymer.

To find the solubility parameter the heat of vaporization has to be determined. Unfortunately the heat of vaporization of a polymer can not be obtained experimentally because polymers decompose before

they vaporize. Therefore the method most often used to determine the cohesive energy densities of polymers is based on the idea that the size of a polymer molecule in solution is at a maximum when the cohesive energy densities of the solvent and polymer are equal.

If the polymer is crosslinked, then a known quantity of a polymer is soaked in different solvents with known solubility parameters. When the degree of swelling of the polymer sample is plotted against the solubility parameters, the maximum of the curve will correspond to the solubility parameter of the polymer.

If the polymer is not crosslinked, then it is dissolved in different solvents with known solubility parameters and the intrinsic viscosity of each solution is determined. The maximum of the curve obtained from the plot of intrinsic viscosity, $[\eta]$, versus δ of solvents should correspond to the solubility parameter of the solvent. The cohesive energy density of a single sample of polyvinyl benzoate was determined by this method. In Table 10 the intrinsic viscosities of polyvinyl benzoate in different solvents at 32.5°C are given and these values are plotted in Figure 7. The polymer used in these measurements was that produced using recipe 65. The experimental data and plots for $[\eta]$ can be found in Tables I to VI in Appendix C.

From the experimental data in this study, the cohesive energy of polyvinyl benzoate was estimated to be 105 cal/cm³. The deviation of acetic acid in Figure 7 could be because of it being a highly associated, essentially nonpolar liquid. Usually there is quite a

TABLE 10
Intrinsic Viscosities and Solubility Parameters
of Polyvinyl Benzoate in Different Solvents

Solvent	δ , (cal/cm ³) ^{1/2}	$[\eta]$, dL/g
m-Xylene	8.8	0.0713
Methyl ethyl ketone	9.3	0.1150
Acetone	9.9	0.1416
Acetic acid	10.1	0.1107
Cyclopentanone	10.4	0.1464
Methyl Benzoate	10.5	0.1424

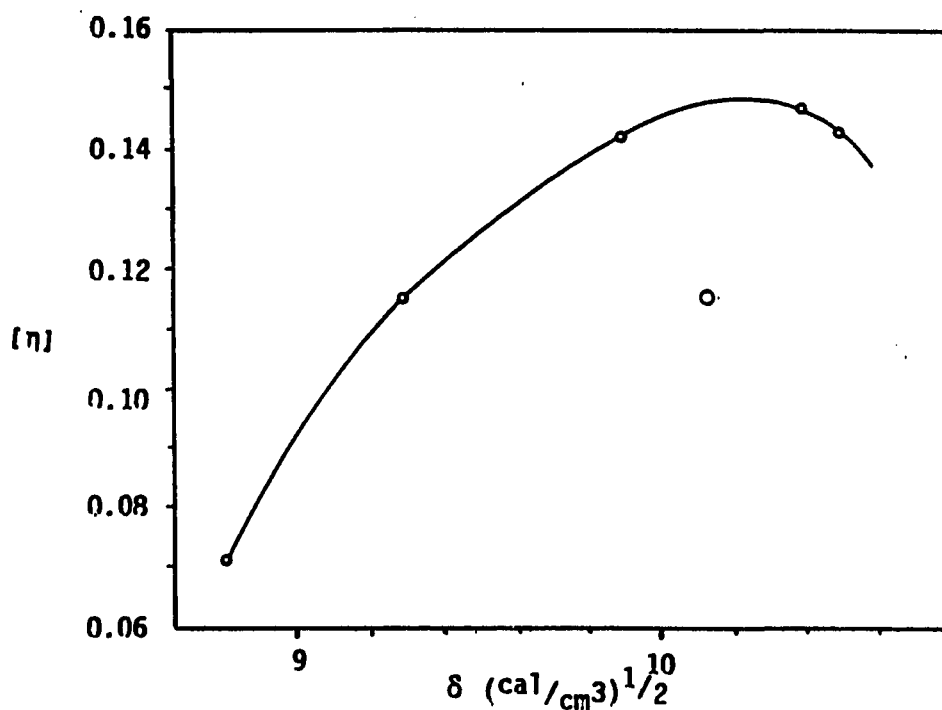


Figure 7. The Solubility Parameter of Polyvinyl Benzoate.

bit of scatter in data of this sort where δ values are used and polarities of solvents or solute are omitted. Equation 13 and 14 assume nonpolar molecules. When either component is polar, or has polar regions within its molecule, deviations from these relationships occur. The manner in which they deviate unfortunately currently can not be predicted with any accuracy.⁴⁰ For this reason when reporting cohesive energy densities, the term "estimated" is more appropriate.

There is a method introduced by Small,⁴¹ for estimating the cohesive energy densities of polymers from a set of additive constants. The values calculated from these constants are reported to be in good agreement with the values obtained from swelling measurements.

The relation between the molar attraction constants, F , which are additive over the molecular formula, and the solubility parameter, δ , is

$$\delta = \frac{\Sigma F}{V} \quad (15)$$

where V is the molar volume. These F values for different groups are given in tables,^{36,37} in units of $(\text{cal}\cdot\text{cc})^{1/2}$.

For the calculation of the cohesive energy density of polyvinyl benzoate the following values of F were used. $-\text{CH}_2 = 133$
 $(\text{cal}\cdot\text{cc})^{1/2}$; $-\text{CH} = 28$ $(\text{cal}\cdot\text{cc})^{1/2}$; phenyl = 735 $(\text{cal}\cdot\text{cc})^{1/2}$; COO
 esters = 310 $(\text{cal}\cdot\text{cc})^{1/2}$. Then ΣF is calculated as 1206 $(\text{cal}\cdot\text{cc})^{1/2}$
 for a polyvinyl benzoate repeating unit. The polyvinyl benzoate
 sample used in cohesive energy density determinations had a

molecular weight of 46000 and 310 repeating units. The molar volume (V) (mL/mole) is found by dividing molecular weight (g/mole), by density (g/mL). The density of similar polymers varies between 0.9 and 1.1 g/mL. In this study the density of polyvinyl benzoate was taken as 1.1 g/mL. With this value the solubility parameter, δ , was calculated to be $9 \text{ (cal/cm}^3\text{)}^{1/2}$.

The experimental value found from Figure 7 is $10.25 \text{ (cal/cm}^3\text{)}^{1/2}$. The use of molar attraction constants give values of δ that are good to one significant figure. Under these conditions the uncertainty in the value of the density will not be significant. The calculated solubility parameter value, $9 \text{ (cal/cm}^3\text{)}^{1/2}$, is in reasonable agreement with the experimental value of $10.25 \text{ (cal/cm}^3\text{)}^{1/2}$.

In both methods of determining δ values there are uncertainties. As stated earlier, factors like steric hindrance, conjugation, and polarity are not considered when molar attraction constants are calculated. In this study only a few solvents were used to find intrinsic viscosities of polyvinyl benzoate. In fact, the intrinsic viscosities of a polymer sample in two solvents with nearly identical solubility parameters can be very different from each other. When a curve is drawn averaging many such points, it may give a cohesive energy density value for that polymer which may be different than the one obtained with only a few solvents. In view of these uncertainties, it can be assumed that these two values of δ , found with two different methods are in fact in the range of

experimental error. Thus the solubility parameter of polyvinyl benzoate is considered to be in the range of 9-10 (cal/cm³)^{1/2}.

Refractive Index Increment of Polyvinyl Benzoate in Solution

The refractive index increment (dn/dc) of polyvinyl benzoate was measured in methyl ethyl ketone and in ethyl acetate. The instrument was calibrated to give the relationship seen below

$$\Delta n = 0.9144 \times 10^{-4} \Delta d$$

where

$$\Delta d = (d_2 - d_1) - (d_2' - d_1')$$

To minimize instrument errors, readings are taken in two cell positions, where the cell is rotated 180° between readings.⁴² The value Δd , is the difference of the solution readings (d), and the solvent reading (d'). The results are shown in Table 11.

TABLE 11

Refractive Index Increment of Polyvinyl Benzoate

Solvent	Δd	$\Delta n \times 10^{-4}$	$C \times 10^{-4}$	dn/dc
Methyl ethyl ketone	1.146	1.0479	7.9777	0.13135
Ethyl acetate	1.194	1.0918	8.9578	0.12190

C stands for concentration in grams of polymer in one milliliter solvent.

Absorption Spectra

The ultraviolet absorption spectrum of polyvinyl benzoate has a maximum absorbance at 254 nm as seen in Figure 8.

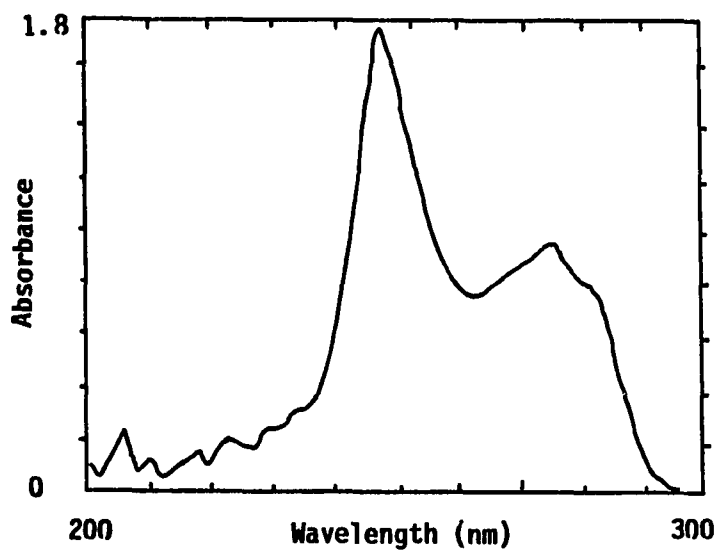


Figure 8. The Ultraviolet Spectrum of Polyvinyl Benzoate.

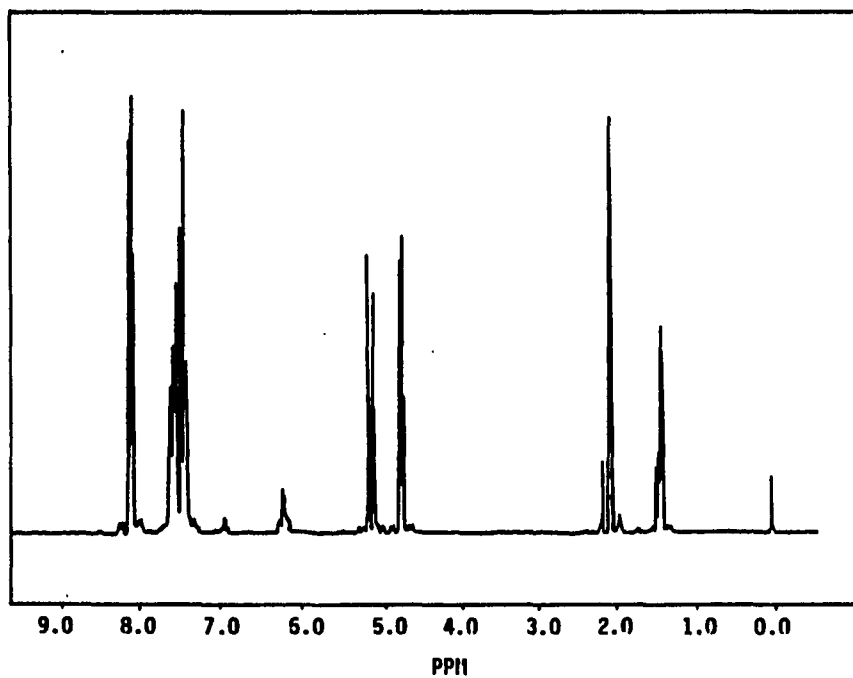


Figure 9. The NMR Spectrum of Vinyl Benzoate.

The nuclear magnetic resonance spectrum of vinyl benzoate is given in Figure 9 and that of polyvinyl benzoate in Figures 10, 11 and 12. There is no significant difference in the spectra of these three polymers obtained from different recipes.

When there is a carbonyl group next to the ring, normally the ortho protons on the benzene ring are shifted downfield from the meta and para protons. Therefore the ortho protons on the benzene ring, next to the ester group show at 7.2ppm, and the CH₂ protons at 2ppm. At this point no explanation is offered for the 8.3ppm and the 2.1ppm peaks in the spectrum of vinyl benzoate.

Unless measurements are made at high temperatures, a lack of chain conformation movements in polymers prevents good resolution in a nuclear magnetic resonance spectrum. The broad absorption bands in the nuclear magnetic resonance spectra of the polymers are due to this property.

The infrared absorption spectra of vinyl benzoate and polyvinyl benzoate can be seen in Figures 13 and 14 respectively. The carbonyl frequency of vinyl esters which normally appears at 1770cm⁻¹, as in vinyl acetate, is shifted to 1740cm⁻¹ because of the conjugation in vinyl benzoate between the phenyl and carbonyl groups. The characteristic stretching frequency of the C-O bond at 1300cm⁻¹ and 1100cm⁻¹, the 1300cm⁻¹ peak being stronger and broader, can also be easily seen. Unfortunately the 2000cm⁻¹ - 1650cm⁻¹ region does not give a clear clue about the substitution pattern on the benzene ring in polyvinyl benzoate.

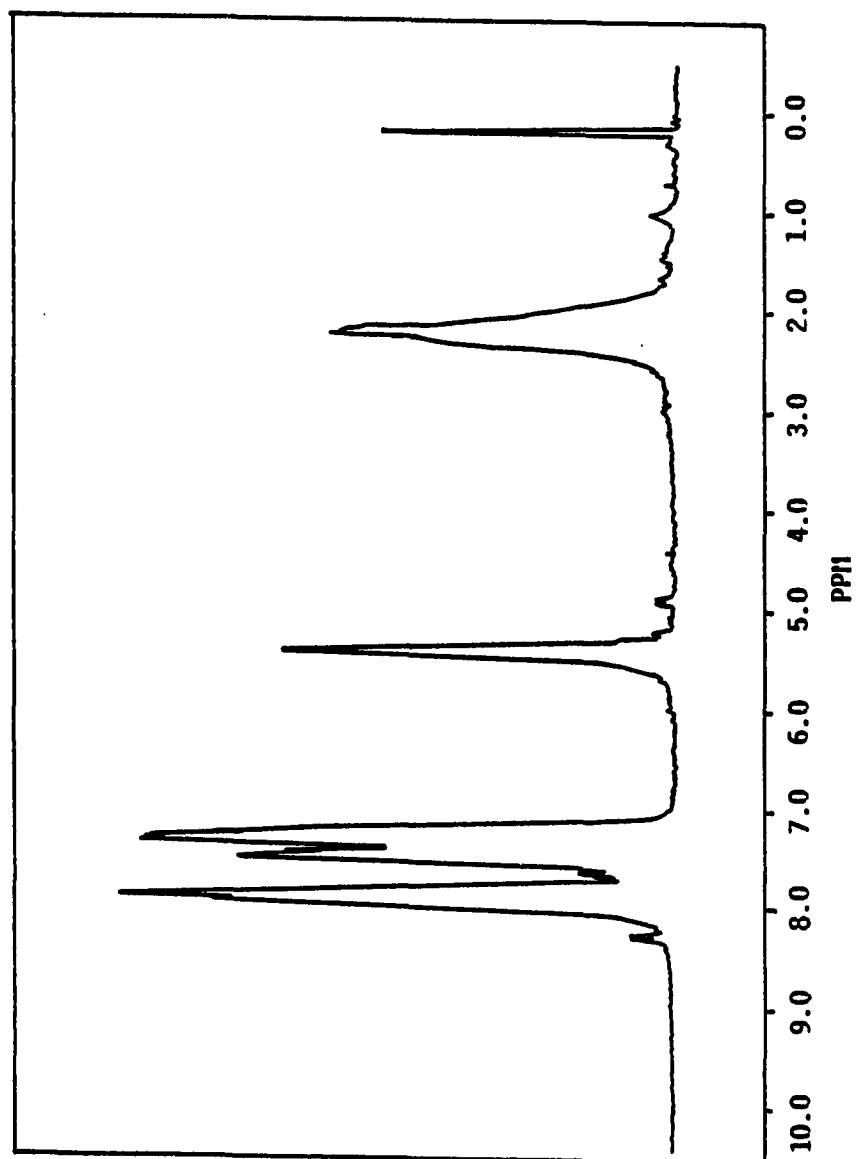


Figure 10. The NMR Spectrum of Polyvinyl Benzoate Obtained from Recipe 40 in CDCl_3 .

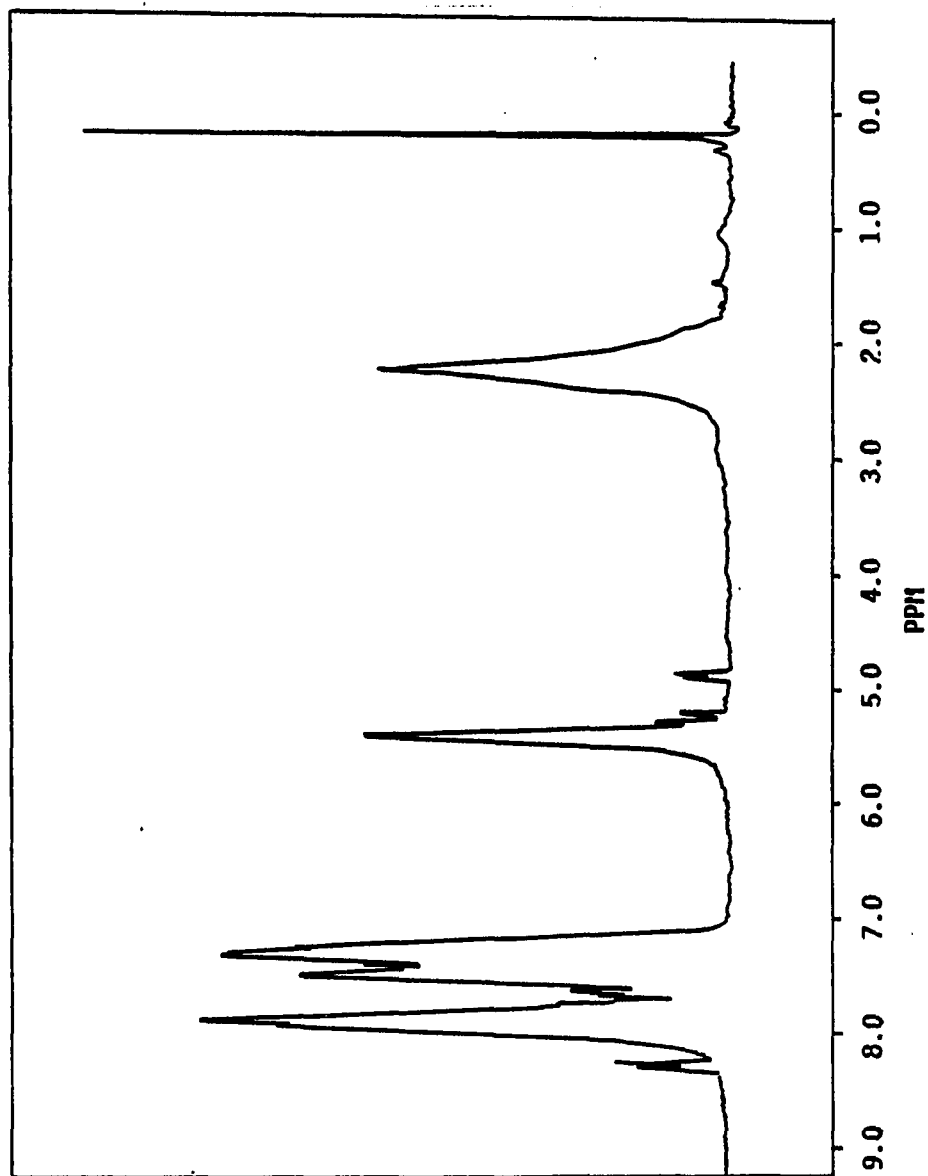


Figure 11. The NMR Spectrum of Polyvinyl Benzoate Obtained from Recipe 43 in CDC13.

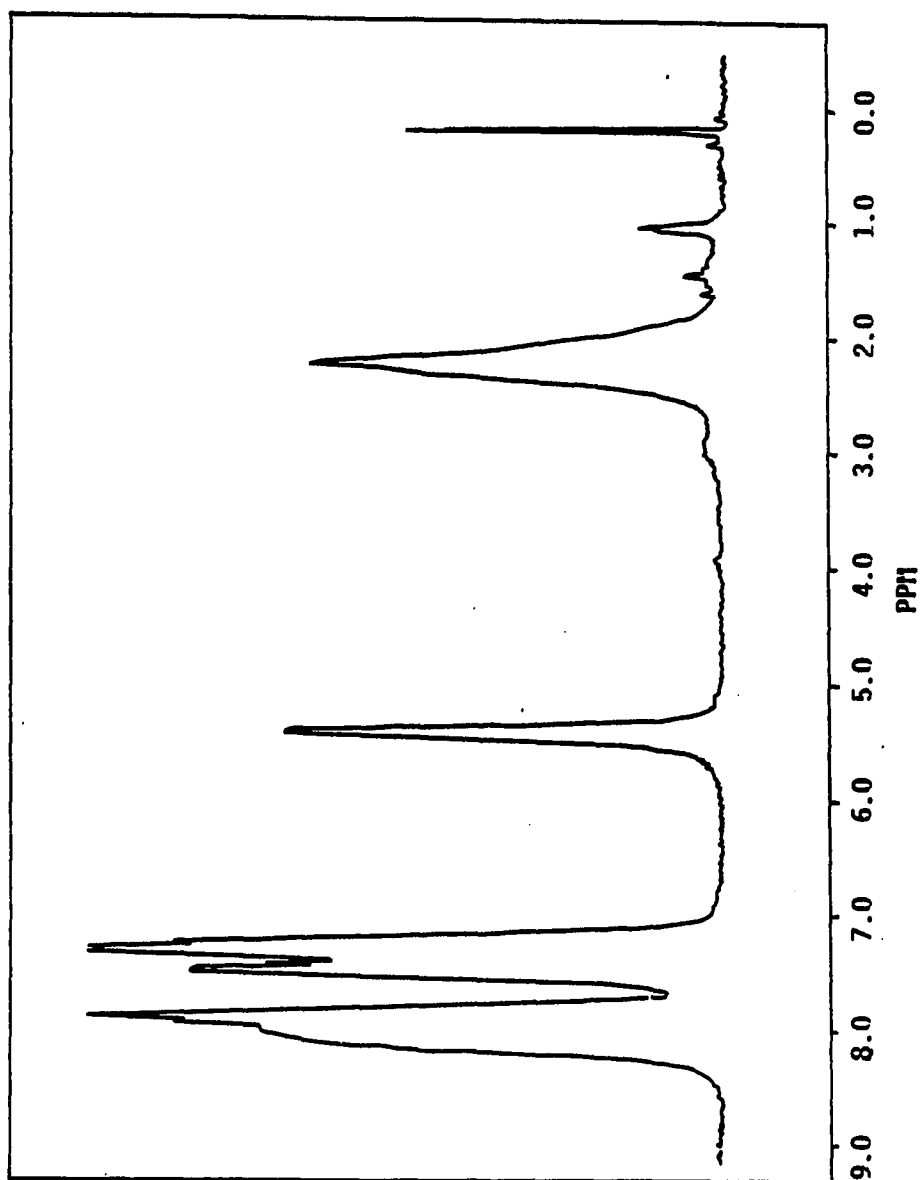


Figure 12. The NMR Spectrum of Polyvinyl Benzoate Obtained from Recipe 69 in CDCl_3 .

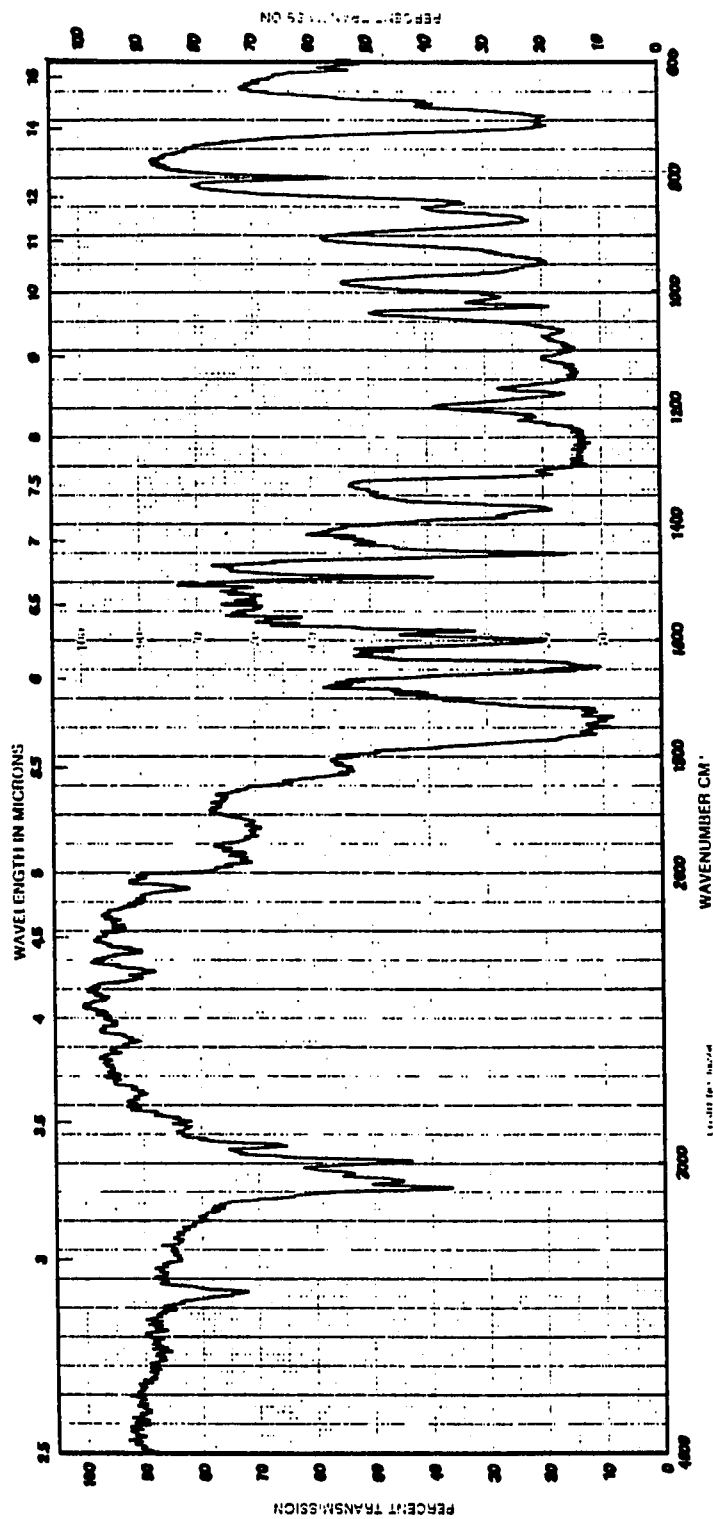


Figure 13. The IR Spectrum of Vinyl Benzoate.

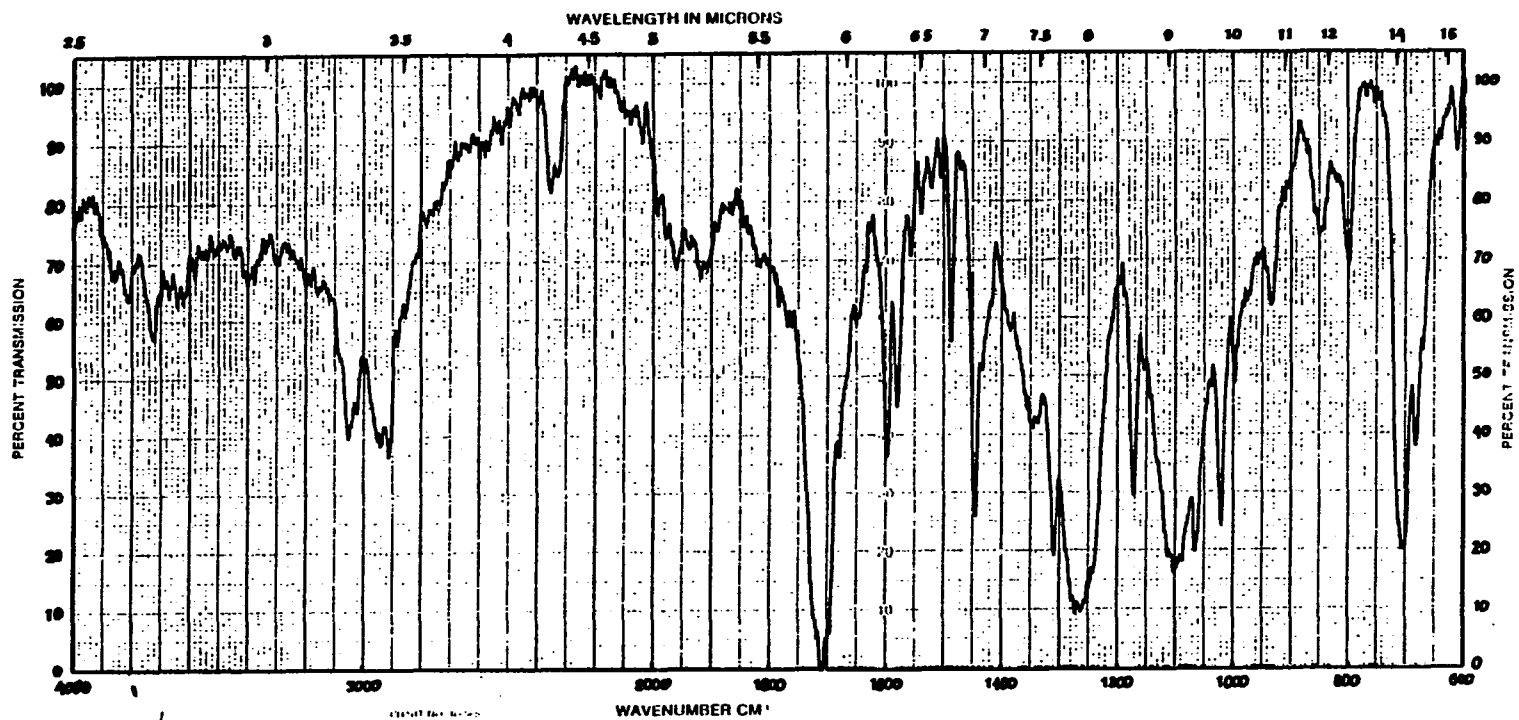


Figure 14. The IR Spectrum of Polyvinyl Benzoate.

SUMMARY AND CONCLUSIONS

A survey of the literature on vinyl benzoate polymerization revealed that polyvinyl benzoate, as expected, was a hard, glassy, crystal clear resin. However the polymerization rate was very low and the polymer was crosslinked to a degree where it was not suitable for commercial applications.

These studies were done with bulk and solution polymerization methods. In hopes of reducing the crosslinking and increasing the polymerization rate and conversion, this study concentrated on the emulsion polymerization technique. In emulsion polymerization the growing polymer particles are isolated from each other; therefore very high molecular weights can be obtained in very short times.

Many different recipes were tried. The highest conversions were obtained from higher temperature polymerizations using mixed anionic and nonionic emulsifiers and potassium peroxydisulfate as an initiator. Increasing emulsifier and initiator concentrations increased the yield. These studies revealed a recipe that gives 95% conversion to polymer in two hours at 75°C, and is shown below.

Vinyl benzoate	100 parts by weight
Water	300 parts by weight
Sodium lauryl sulfate	3 parts by weight
Emulphogene BC-840	1 part by weight
Potassium peroxydisulfate	0.5 parts by weight
Dodecyl mercaptan	0.1 parts by weight
Temperature	75°C

The best method to synthesize large amounts of vinyl benzoate for industrial applications was reported to be the gas phase reaction of benzoic acid and acetylene, using cadmium acetate catalysts. For research purposes the vinyl interchange reaction between benzoic acid and vinyl acetate was used. This method give 80% yields in three hours at 75°C and does not require complicated set ups and expensive equipment.

The viscosity average molecular weight studies did not indicate a very large change in molecular weights with changing emulsifiers, initiators and temperatures.

To aid further research on this polymer the solubility parameter, refractive index increment and the ultraviolet, infrared and nuclear magnetic resonance spectra of polyvinyl benzoate are also given.

From the results of this study the following conclusions are made.

1. Increasing the emulsifier concentration increased the extent of conversion. Also mixed anionic and nonionic emulsifiers were more effective than only anionic emulsifiers in increasing the conversion. The best combination was 75% sodium lauryl sulfate and 25% Emulphogene BC-840.

2. Increasing the initiator concentration increases the extent of conversion. This supports the existing theory. However redox

recipes were found to be ineffective, giving very low conversions. Potassium peroxydisulfate gave the highest conversions.

3. Polyvinyl benzoate obtained from the recipe given above gave molecular weights in the range of 30000 to 60000.

4. Cohesive energy density studies of this polymer gave a solubility parameter (δ) value of $10.2 \text{ (cal/cm}^3)^{1/2}$. This value is in good agreement with the calculated value of $9 \text{ (cal/cm}^3)^{1/2}$ because the difference is within the limits of the uncertainties in the determinations of these values in both methods.

RECOMMENDATIONS

As the emulsion polymerization of vinyl benzoate has not been studied previously, it is worth while to expand this present work and look into its mechanism in more detail.

Judging from the rate studies that show some deviation from general emulsion polymerization results, there is a possibility of some polymerization occurring in the aqueous phase. This could lead to a fraction with very different molecular weights than that in micelle particles. Therefore a molecular weight distribution study will clarify this point. In addition to this more detailed and extensive rate study should be made to determine \bar{n} , the number of free radicals in a polymer particle, and the functionality of the particle number, N , to the initiator concentration, R_i , and emulsifier concentration, S . The results of such a study may help to explain the unusual behavior of polyvinyl benzoate in polymerizations and lead to a better understanding of its polymerization behavior.

Possibilities of increasing the molecular weights of polyvinyl benzoate polymers by reducing the amount of chain transfer agent should be investigated. Chain transfer agents reduce molecular weights by shortening chain lengths. In this study this was a desired effect hoping it would reduce crosslinking. However there is no evidence indicating an increase in crosslinking with decreasing amounts of chain transfer agent. Therefore by decreasing

the amount of the chain transfer agent higher molecular weights can be obtained. If there is an increase in crosslinking this can be identified by hydrolysis studies. The side chains that result from the phenyl ring participation in the free radical polymerizations can be hydrolyzed. This will give a sharp decrease in the molecular weights and the extent of the decrease will give an idea about the extent of crosslinking in the polymer.

There are many combinations of initiators and emulsifiers that are possible in emulsion polymerizations. It might be possible to get higher conversions and higher molecular weights with different initiator and emulsifier ratios, or anionic-nonionic emulsifier mixtures for emulsifier systems. This area is always open to improvements, therefore it is suggested for further research.

Steam distillation of residual unpolymerized monomer from the latex is a procedure frequently used in industry. This procedure should be tried with polyvinyl benzoate latex. Even though it often requires the use of additional latex stabilizers, it may be desirable as a method of monomer removal from polyvinyl benzoate for industrial applications.

The polyvinyl benzoate obtained by emulsion polymerization in this study does not have good film forming characteristics at room temperature. All attempts to cast a film from the solution of the purified polymer, and directly from the latex, failed. A flaky deposit was formed that crumbles under the attempts to remove the

film from the casting substrate. This characteristic is typical for low molecular weight polymers, especially those that have a glass transition temperature (T_g) above room temperature. It is also characteristic of films cast from latexes consisting of cross-linked or highly branched particles. Therefore further studies on methods in orienting the polymer and determining the T_g of polyvinyl benzoate polymers, obtained from emulsion polymerizations, will provide useful information for applications.

APPENDICES

Appendix A
Polymerization Recipes

TABLE A-I
Polymerizations Using Potassium Peroxydisulfate as Initiator

Component	Recipe Number							
	1	2	3	4	5	6	7	8
Vinyl benzoate, g	32.640	8.001	20.010	15.001	10.003	10.000	10.011	10.005
Water, g	57.750	14.403	36.100	27.000	20.015	20.000	20.035	18.033
Potassium peroxydisulfate, g	0.065	0.016	0.040	0.024	0.025	0.025	0.025	0.009
Sodium lauryl sulfate, g	1.630	0.400	1.002	0.750	0.601	0.025	0.349	0.400
Emulphogene BC-840, g	—	—	—	—	—	0.150	—	—
Potassium thiosulfate, g	—	—	—	—	—	—	—	0.014
Potassium hydrogen sulfite, g	—	—	—	0.024	0.010	0.010	0.010	—
Iron(II) sulfate, g	—	—	—	—	0.003	*0.003	*0.028	—
Ethylenediamine-tetraacetic acid, g	—	—	—	—	0.010	*0.010	—	—
Sodium pyrophosphate, g	—	—	—	—	—	—	*0.045	—
Copper(II) sulfate, g	—	—	—	—	—	—	—	0.0050
Glucose, g	—	—	—	—	0.100	0.100	0.100	—
Dodecyl mercaptan, g	—	—	0.050	—	0.024	0.024	0.024	—
Time, h	20	12	18	18	12	18	23	20
Temperature, °C	50	71	45	50	60	0	0	0
Conversion, %	26	35	57	18	38	8	4	6

* These compounds are mixed in solution prior to adding to charge.

TABLE A-II
Polymerizations Using Cumene Hydroperoxide as Initiator

Component	9	10	Recipe 11	Number 12	13	14	15
Vinyl benzoate, g	10.000	10.002	10.005	10.006	10.000	10.040	10.001
Water, g	18.054	18.001	18.040	20.004	18.054	19.003	18.000
Sodium lauryl sulfate, g	0.601	0.500	0.500	0.502	0.300	0.500	0.302
Emulphogene BC-840, g	—	—	—	—	0.250	—	0.200
Cumene hydroperoxide, g	0.050	0.010	0.011	0.017	0.005	0.017	0.017
Iron(II) sulfate, g	—	0.028	*0.028	0.028	*0.010	0.008	0.008
Ethylenediaminetetraacetic acid, g	—	0.011	*0.100	—	—	—	—
Sodium pyrophosphate, g	—	—	—	0.045	*0.100	0.100	0.100
Sodium sulfide, g	—	—	—	—	—	0.006	0.007
Glucose, g	—	0.101	0.100	—	—	—	—
Fructose, g	—	—	—	—	—	1.001	—
Hydroxy acetone, g	—	—	—	—	0.007	—	—
Potassium chloride, g	—	0.050	0.050	—	—	—	—
Potassium hydroxide, g	—	0.009	0.090	—	—	—	—
Dodecyl mercaptan, g	0.040	0.024	0.024	0.025	0.020	0.035	—
Time, h	19	12	18	23	20	19	19
Temperature, °C	50	0	0	0	0	36	0
Conversion, %	27	8	9	8	7	7	5

* These compounds are mixed in solution prior to adding to charge.

TABLE A-III
Polymerizations Using Potassium Dichromate, Air and Dibenzoyl Peroxide as Initiator

Component	Recipe Number			
	16	17	18	19
Vinyl benzoate, g	7.001	10.000	10.050	10.004
Water, g	12.600	18.231	20.008	18.003
Sodium lauryl sulfate, g	0.200	0.600	0.600	0.300
Emulphogene BC-840, g	0.151	—	—	0.250
Potassium dichromate, g	0.021	0.030	—	—
Arsenic trioxide, g	0.007	0.010	—	—
Dibenzoyl peroxide, g	—	—	—	0.009
Iron(II) sulfate, g	0.007	—	0.005	0.010
Sodium pyrophosphate, g	—	—	0.500	0.300
Air, mL	—	—	20	—
Fructose, g	—	—	—	0.010
Dodecyl mercaptan, g	0.018	0.040	0.010	0.040
Time, h	20	19	19	19
Temperature, °C	56	56	50	50
Conversion, %	6.5	8	9	7

TABLE A-IV
Polymerizations Using Dibenzoyl Peroxide as Initiator

Component	Recipe Number					
	20	21	22	23	24	25
Vinyl benzoate, g	2.447	2.4310	5.335	5.335	5.335	5.335
Water, g	7.465	7.4650	14.835	14.957	14.835	14.957
Sodium lauryl sulfate, g	0.025	0.0250	0.500	0.500	0.500	0.500
Dibenzoyl peroxide, g	0.007	0.0125	0.025	0.025	0.025	0.025
Dimethyl aniline, g	—	—	0.292	0.150	—	—
Caffeine, g	—	—	—	—	0.437	0.240
Dodecyl mercaptan, g	0.013	0.0130	0.053	0.053	0.039	0.053
Time, h	11	11	10	10	10	10
Temperature, °C	60	60	60	60	60	60
Conversion, %	28	16	4	3	2.5	15

TABLE A-V
Polymerizations of Styrene and Vinyl Acetate Using
Potassium Peroxydisulfate as Initiator

Component	Recipe Number	
	26	27
Styrene, g	4.928	—
Vinyl acetate, g	—	4.956
Water, g	14.925	14.963
Sodium lauryl sulfate, g	0.500	0.500
Potassium peroxydisulfate, g	0.013	0.013
Dodecyl mercaptan, g	0.026	0.026
Time, h	14	14
Temperature, °C	60	60
Conversion, %	99	98

TABLE A-VI
Effect of Temperature Using Sodium Lauryl Sulfate as Emulsifier

Component	Recipe Number			
	28	29	30	31
Vinyl benzoate, g	10.010	10.358	10.341	10.040
Water, g	18.008	18.511	18.053	18.000
Sodium lauryl sulfate, g	0.500	0.500	0.500	0.500
Potassium peroxydisulfate, g	0.025	0.025	0.025	0.025
Dodecyl mercaptan, g	0.040	0.040	0.040	0.040
Time, h	21	21	12	12
Temperature, °C	50	60	70	80
Conversion, %	28	84	74	90

TABLE A-VII
Effect of Temperature Using Mixtures
of Anionic and Nonionic Emulsifier

Component	Recipe Number			
	32	33	34	35
Vinyl benzoate, g	10.231	10.325	10.101	10.054
Water, g	18.315	18.000	18.031	18.431
Sodium lauryl sulfate, g	0.300	0.301	0.300	0.300
Emulphogene BC-840, g	0.250	0.250	0.250	0.250
Potassium peroxydisulfate, g	0.030	0.030	0.030	0.030
Dodecyl mercaptan, g	0.040	0.040	0.040	0.040
Time, h	21	21	12	12
Temperature, °C	50	60	70	80
Conversion, %	33	88	83	94

TABLE A-VIII
Effect of Temperature Using Higher Concentrations
of Sodium Lauryl Sulfate as Emulsifier

Component	Recipe Number			
	36	37	38	39
Vinyl benzoate, g	10.041	10.034	10.000	10.030
Water, g	18.348	18.031	18.040	18.005
Sodium lauryl sulfate, g	1.500	1.500	1.500	1.500
Potassium peroxydisulfate, g	0.025	0.025	0.025	0.025
Dodecyl mercaptan, g	0.040	0.040	0.040	0.040
Time, h	21	21	12	12
Temperature, °C	50	60	70	80
Conversion, %	87	90	89	90

TABLE A-IX
Effect of Sodium Hydrogen Sulfite Concentration Using a Redox Recipe

Component	Recipe Number			
	40	41	42	43
Vinyl benzoate, g	10.005	10.030	10.041	10.003
Water, g	18.548	18.600	18.040	18.005
Sodium lauryl sulfate, g	0.504	0.500	0.500	0.501
Potassium peroxydisulfate, g	0.025	0.025	0.025	0.025
Sodium hydrogen sulfate, g	0.025	0.015	0.040	0.090
Dodecyl mercaptan, g	0.040	0.040	0.040	0.040
Time, h	21	21	21	21
Temperature, °C	50	50	50	50
Conversion, %	38	39	34	51

TABLE A-X
Effect of Temperature on Polymerization
Using Cumene Hydroperoxide as Initiator

Component	Recipe Number			
	44	45	46	47
Vinyl benzoate, g	10.004	10.000	10.004	10.060
Water, g	18.037	18.058	18.049	18.009
Sodium lauryl sulfate, g	0.402	0.430	0.808	0.800
Emulphogene BC-840, g	0.231	0.215	0.587	0.430
Cumene hydroperoxide, g	0.050	0.050	0.050	0.050
Dodecyl mercaptan, g	0.040	0.040	0.040	0.040
Time, h	21	21	21	21
Temperature, °C	60	80	60	80
Conversion, %	4	88	12	74

TABLE A-XI
Polymerizations at Increasing Temperature Using Nonionic Emulsifier

Component	Recipe Number	
	48	49
Vinyl benzoate, g	10.031	10.049
Water, g	18.754	18.840
Potassium peroxydisulfate, g	0.025	0.030
Emulphogene BC-840, g	1.099	1.070
Temperature, °C	60	75
Conversion, %, at 3h	1	8
Conversion, %, at 8h	3	45
Conversion, %, at 12h	51	50

TABLE A-XII
Polymerizations Using Dodecyl Benzene Sulfonate as Emulsifier

Component	Recipe Number		
	50	51	52
Vinyl benzoate, g	10.063	10.044	10.001
Water, g	18.041	18.039	18.029
Dodecyl benzene sulfonate, g	1.025	1.025	0.785
Emulphogene BC-840, g	—	—	0.651
Potassium peroxydisulfate, g	0.035	0.035	0.025
Sodium hydrogen sulfite, g	—	—	0.030
Dodecyl mercaptan, g	0.050	0.050	0.040
Temperature, °C	60	75	60
Conversion, %, at 3h	10	64	5
Conversion, %, at 8h	31	86	31
Conversion, %, at 12h	51	91	57

TABLE A-XIII
The Effect of Changing Component Ratios, Time and Temperature
on Polymerizations Using Mixed Emulsifiers

Component	Recipe Number					
	53	54	55	56	57	58
Vinyl benzoate, g	10.057	10.004	10.051	10.065	10.004	10.037
Water, g	30.008	30.005	18.049	18.247	30.341	30.045
Sodium lauryl sulfate, g	0.510	0.510	0.800	0.803	0.802	0.822
Emulphogene BC-840, g	0.500	0.480	0.500	0.555	0.545	0.596
Potassium peroxydisulfate, g	0.030	0.030	0.025	0.025	0.025	0.025
Sodium hydrogen sulfite, g	—	—	0.025	0.025	0.025	0.025
Dodecyl mercaptan, g	0.050	0.050	0.040	0.040	0.040	0.040
Temperature, °C	60	75	60	75	60	75
Conversion, %, at 3h	4.5	88	8	51	6	44
Conversion, %, at 8h	21	89	84	73	87	87
Conversion, %, at 12h	80	90	90	85	89	90

TABLE A-XIV
Effect of Increasing Emulsifier Concentration

Component	Recipe Number		
	59	60	61
Vinyl benzoate, g	16.0680	16.0680	21.4240
Water, g	44.8650	44.8650	59.8200
Sodium lauryl sulfate, g	0.7571	1.5038	4.0007
Potassium peroxydisulfate, g	0.4008	0.4008	0.5010
Dodecyl mercaptan, g	0.0660	0.0660	0.0924
Time, h	18	18	18
Temperature, °C	75	75	75
Conversion, %	85	96	84

TABLE A-XV
Effect of Increasing Initiator Concentration

Component	Recipe Number		
	62	63	64
Vinyl benzoate, g	16.0680	16.0680	21.4240
Water, g	44.8650	44.8620	59.8200
Sodium lauryl sulfate, g	1.4975	1.4975	2.0070
Potassium peroxydisulfate, g	0.2004	0.4008	1.0020
Dodecyl mercaptan, g	0.0660	0.0660	0.0924
Time, h	18	18	18
Temperature, °C	75	75	75
Conversion, %	85	85	88

TABLE A-XVI
Effect of Increasing Emulsifier Concentration

Component	Recipe Number		
	65	66	67
Vinyl benzoate, g	21.4580	21.4580	21.4580
Water, g	59.6440	59.6440	59.6440
Sodium lauryl sulfate, g	0.9975	2.0010	3.9900
Potassium peroxydisulfate, g	0.0500	0.0500	0.0500
Dodecyl mercaptan, g	0.0924	0.0924	0.0924
Time, h	10	10	10
Temperature, °C	60	60	60
Conversion, %	40	50	60

TABLE A-XVII
Effect of Increasing Initiator Concentration

Component	Recipe Number		
	68	69	70
Vinyl benzoate, g	21.4580	21.4580	21.4580
Water, g	59.6691	59.6440	59.5940
Sodium lauryl sulfate, g	2.0010	2.0000	2.0040
Potassium peroxydisulfate, g	0.0250	0.0500	0.1000
Dodecyl mercaptan, g	0.0924	0.0924	0.0924
Time, h	10	10	10
Temperature, °C	60	60	60
Conversion, %	32	50	80

Appendix B

Viscosity Measurements of Polyvinyl Benzoate for Determinations of Molecular Weights in Methyl Ethyl Ketone at 30°C

Table B-I
Recipe 65

Concentration g/dL	Time s	η_{rel}	$\ln \eta_{rel}/c$ dL/g	η_{sp}/c dL/g
pure solvent	137.00	—	—	—
0.750	149.40	1.09051	0.11553	0.12068
1.200	157.40	1.14891	0.11567	0.12409
1.500	162.95	1.18942	0.11564	0.12628
1.875	170.15	1.24197	0.11557	0.12905
2.000	172.60	1.25985	0.11548	0.12993

Table B-II
Recipe 66 and 69

Concentration g/dL	Time s	η_{rel}	$\ln \eta_{rel}/c$ dL/g	η_{sp}/c dL/g
pure solvent	136.5	—	—	—
0.750	146.8	1.0755	0.09700	0.10060
1.200	153.7	1.1260	0.09890	0.10500
1.500	159.1	1.1656	0.10210	0.11040
1.875	166.3	1.2183	0.10530	0.11640
2.000	168.6	1.2352	0.10560	0.11760

Table B-III

Recipe 67

Concentration g/dL	Time s	η_{rel}	$\ln \eta_{rel}/c$ dL/g	η_{sp}/c dL/g
pure solvent	136.90	—	—	—
0.750	146.90	1.07305	0.09400	0.09739
1.200	153.30	1.11980	0.09429	0.09983
1.500	157.70	1.15194	0.09430	0.10129
1.875	163.50	1.19430	0.09470	0.10363
2.000	165.45	1.20855	0.09471	0.10427

Table B-IV

Recipe 68

Concentration g/dL	Time s	η_{rel}	$\ln \eta_{rel}/c$ dL/g	η_{sp}/c dL/g
pure solvent	136.90	—	—	—
0.750	147.60	1.07816	0.10034	0.10421
1.200	154.50	1.12856	0.10079	0.10713
1.500	159.30	1.16362	0.10103	0.10908
1.875	165.55	1.20928	0.10135	0.11161
2.000	167.70	1.22498	0.10146	0.11249

Table B-V

Recipe 70

Concentration g/dL	Time s	η_{rel}	$\ln \eta_{rel}/c$ dL/g	η_{sp}/c dL/g
pure solvent	137.30	—	—	—
1.250	155.60	1.13340	0.10010	0.10660
2.000	168.10	1.22430	0.10120	0.11220
2.500	177.20	1.29060	0.10200	0.11620
3.125	189.20	1.37800	0.10260	0.12100

Table B-VI

Recipe 51

Concentration g/dL	Time s	η_{rel}	$\ln \eta_{rel}/c$ dL/g	η_{sp}/c dL/g
pure solvent	136.70	—	—	—
0.750	153.10	1.11997	0.15107	0.15996
1.200	163.90	1.19898	0.15122	0.16581
1.500	171.40	1.25384	0.15081	0.16923
1.714	177.10	1.29554	0.15104	0.17240
1.875	181.35	1.32663	0.15074	0.17420

Table B-VII
Recipe 54

Concentration g/dL	Time s	η_{rel}	$\ln \eta_{rel}/C$ dL/g	η_{sp}/C dL/g
pure solvent	136.60	—	—	—
0.750	152.80	1.11859	0.14943	0.15813
1.200	163.55	1.19729	0.15005	0.16441
1.500	171.20	1.25329	0.15052	0.16886
1.875	181.40	1.32796	0.15128	0.17490
2.000	185.00	1.35432	0.15165	0.17716

Table B-VIII
Recipe 73

Concentration g/dL	Time s	η_{rel}	$\ln \eta_{rel}/C$ dL/g	η_{sp}/C dL/g
pure solvent	136.60	—	—	—
0.750	148.75	1.08895	0.11361	0.11859
1.200	156.60	1.14641	0.11386	0.12201
1.500	162.10	1.18668	0.11410	0.12445
1.875	169.10	1.23792	0.11383	0.12689
2.000	171.60	1.25622	0.11405	0.12811

Table B-IX
Polystyrene

Concentration g/dL	Time s	η/η_0	$\ln \eta_{rel}/c$ dL/g	η_{sp}/c dL/g
pure solvent	127.95	—	—	—
0.200	137.70	1.07620	0.36720	0.38100
0.400	148.20	1.15830	0.36730	0.39580
0.600	159.55	1.24700	0.36790	0.41170
0.800	171.85	1.34310	0.36870	0.42890
1.000	185.10	1.44660	0.36930	0.44660

Table B-X
Polyvinyl Acetate

Concentration g/dL	Time s	η/η_0	$\ln \eta_{rel}/c$ dL/g	η_{sp}/c dL/g
pure solvent	96.00	—	—	—
0.200	103.70	1.0802	0.38580	0.40100
0.400	111.50	1.1615	0.37430	0.40380
0.600	119.40	1.2437	0.36350	0.40620
0.800	127.35	1.3266	0.35330	0.40820
1.000	135.35	1.4099	0.34350	0.40990

Appendix C

**Intrinsic Viscosities of Polyvinyl Benzoate
Obtained from Recipe 65 at 32.5°C
for the Determination of Cohesive Energy Density**

Table C-I
Solvent m-Xylene

Concentration g/dL	Time s	η_{rel}	$\ln \eta_{rel}/c$ dL/g	η_{sp}/c dL/g
pure solvent	190.00	—	—	—
0.750	202.15	1.06395	0.08265	0.08526
1.200	211.40	1.11263	0.08894	0.09386
1.500	218.50	1.15000	0.09317	0.10000
1.875	228.45	1.20237	0.09829	0.10793
2.000	231.90	1.22053	0.09964	0.11026

Table C-II
Solvent Methyl Ethyl Ketone

Concentration g/dL	Time s	η_{rel}	$\ln \eta_{rel}/c$ dL/g	η_{sp}/c dL/g
pure solvent	133.45	—	—	—
0.750	145.60	1.09205	0.11618	0.12139
1.200	153.50	1.15024	0.11665	0.12520
1.500	159.10	1.19221	0.11720	0.12814
1.875	166.40	1.24691	0.11769	0.13168
2.000	168.90	1.26564	0.11779	0.13283

Table C-III
Solvent Acetone

Concentration g/dL	Time s	η_{rel}	$\ln \eta_{rel}/c$ dL/g	η_{sp}/c dL/g
pure solvent	111.30	—	—	—
0.750	123.60	1.11051	0.13976	0.14735
1.200	131.45	1.18104	0.13866	0.15087
1.500	136.90	1.23001	0.13801	0.15334
1.875	143.90	1.29290	0.13701	0.15621
2.000	146.30	1.31447	0.13672	0.15723

Table C-IV
Solvent Acetic Acid

Concentration g/dL	Time s	η_{rel}	$\ln \eta_{rel}/c$ dL/g	η_{sp}/c dL/g
pure solvent	297.70	—	—	—
0.750	323.50	1.08666	0.11082	0.11555
1.200	339.85	1.14159	0.11035	0.11799
1.500	351.70	1.18139	0.11113	0.12093
1.875	366.30	1.23043	0.11060	0.12289
2.000	371.40	1.24756	0.11060	0.12378

Table C-V
Solvent Cyclopentanone

Concentration g/dL	Time s	η_{rel}	$\ln \eta_{rel}/c$ dL/g	η_{sp}/c dL/g
pure solvent	323.20	—	—	—
0.750	360.70	1.11603	0.14637	0.15470
1.200	385.10	1.19152	0.14603	0.15960
1.500	402.20	1.24443	0.14579	0.16295
1.875	424.60	1.31373	0.14553	0.16733
2.000	432.50	1.33818	0.14566	0.16909

Table C-VI
Solvent Methyl Benzoate

Concentration g/dL	Time s	η_{rel}	$\ln \eta_{rel}/c$ dL/g	η_{sp}/c dL/g
pure solvent	443.70	—	—	—
0.750	493.70	1.11294	0.14267	0.15059
1.200	526.30	1.18643	0.14246	0.15536
1.500	549.25	1.23817	0.14242	0.15878
1.875	579.40	1.30613	0.14244	0.16327
2.000	589.50	1.32890	0.14217	0.16445

Appendix D

Conversion versus Time Plots of Kinetic Experiments at 60°C

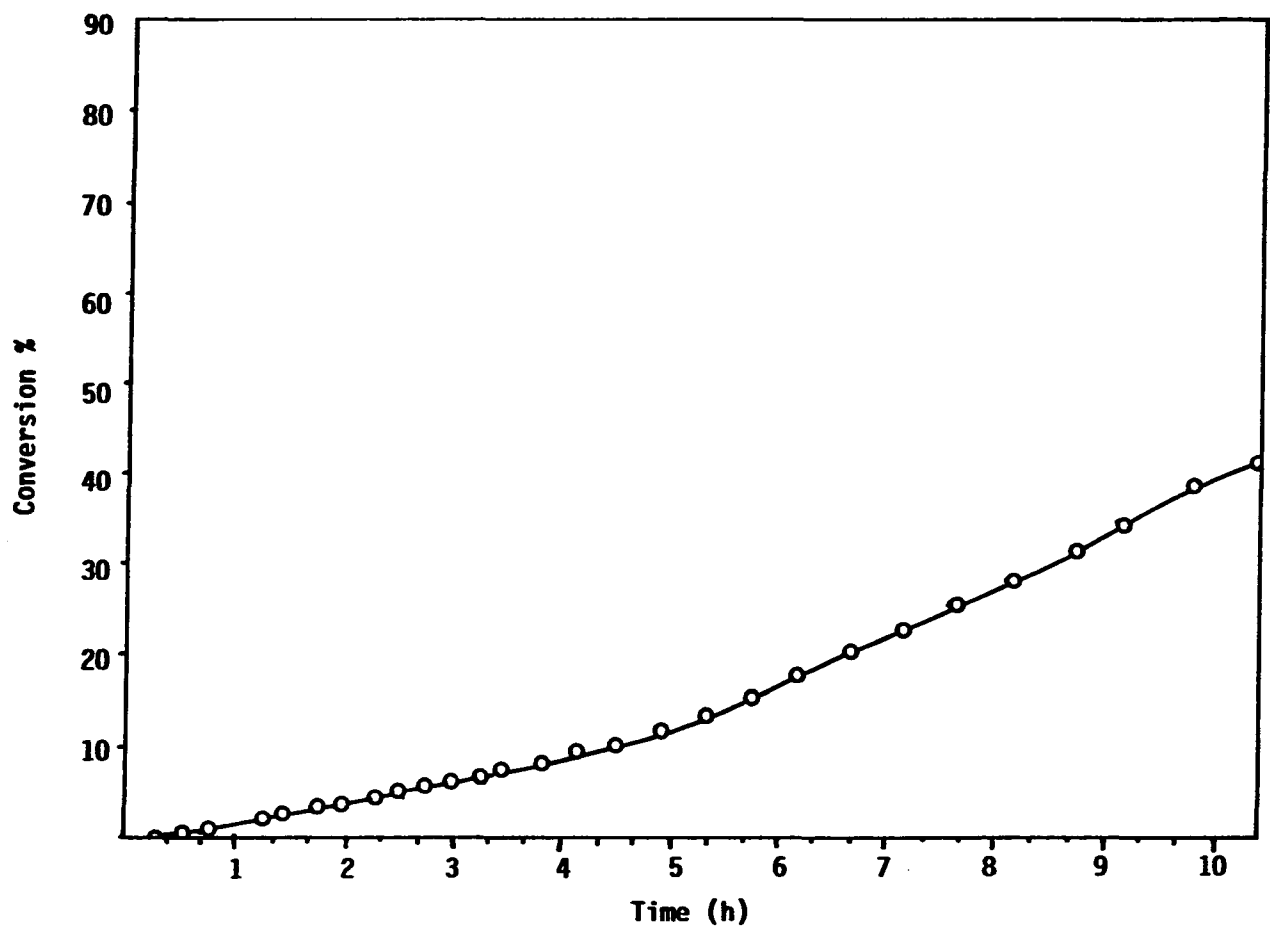


Figure D-1. Conversion vs Time plot of Experiment 65, with Decreased Emulsifier Concentration.

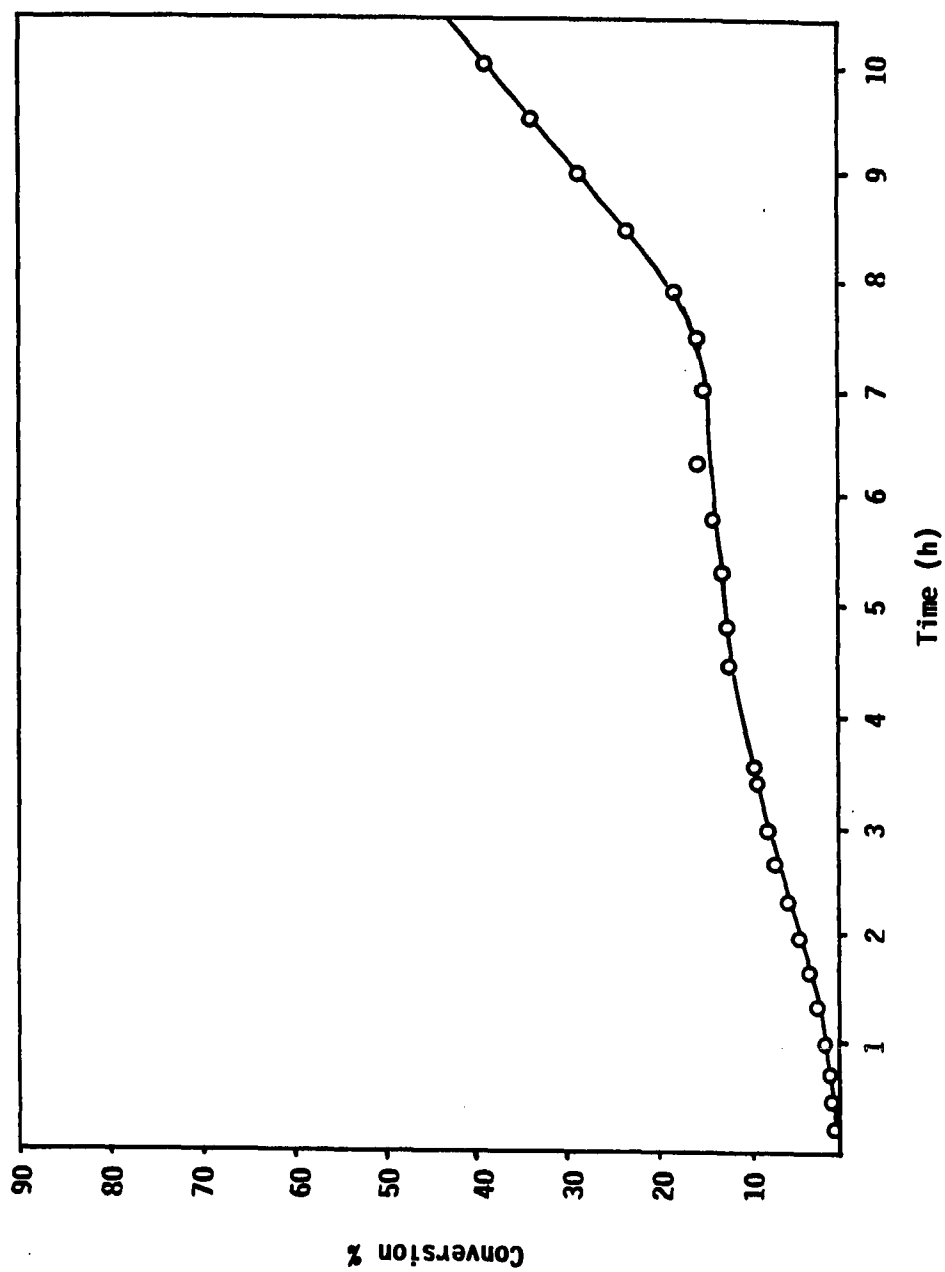


Figure D-2. Conversion vs. Time Plot of Recipe 65 with Decreased Emulsifier Concentration.

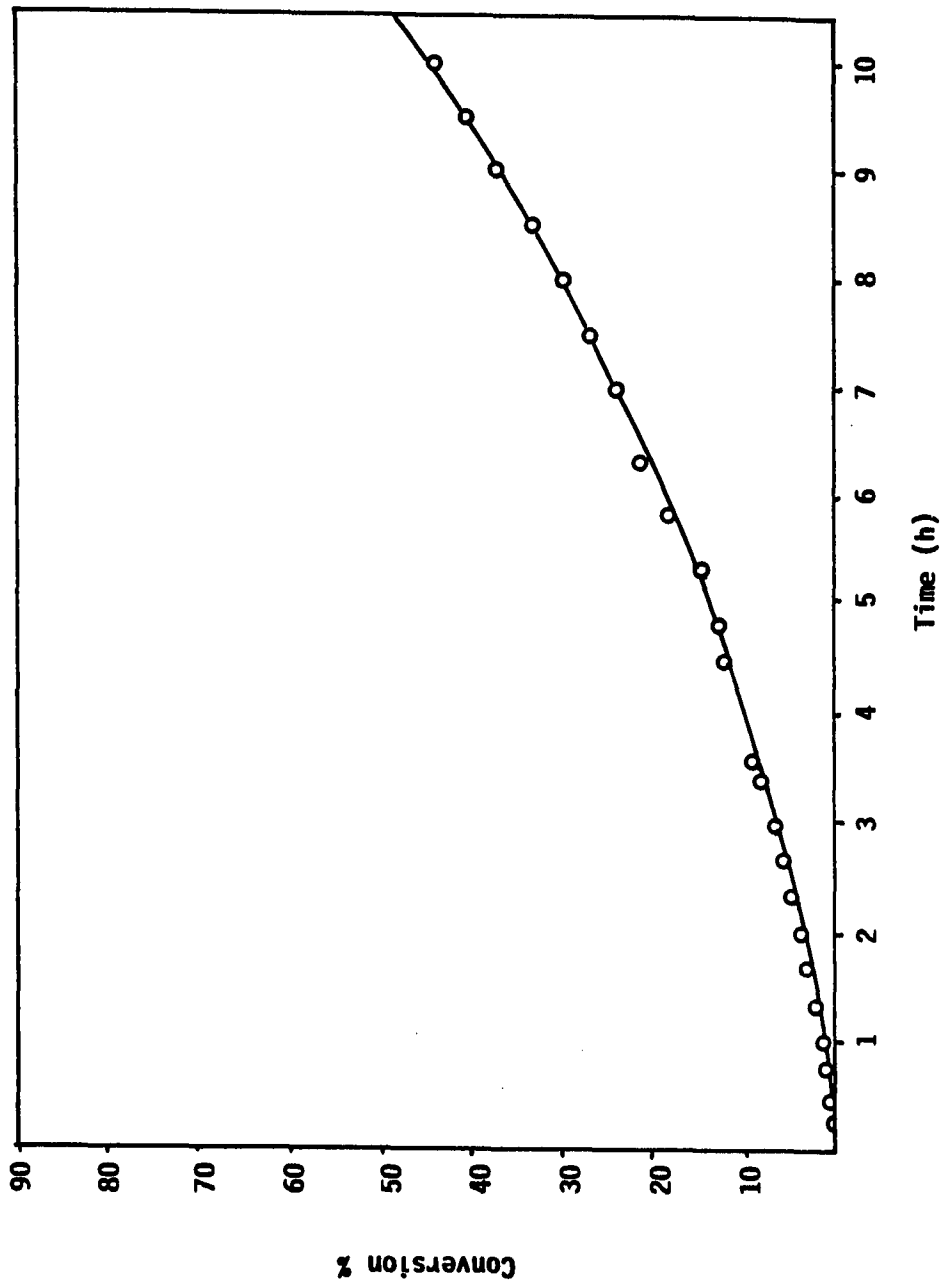


Figure D-3. Conversion vs. Time Plot of Recipe 66.

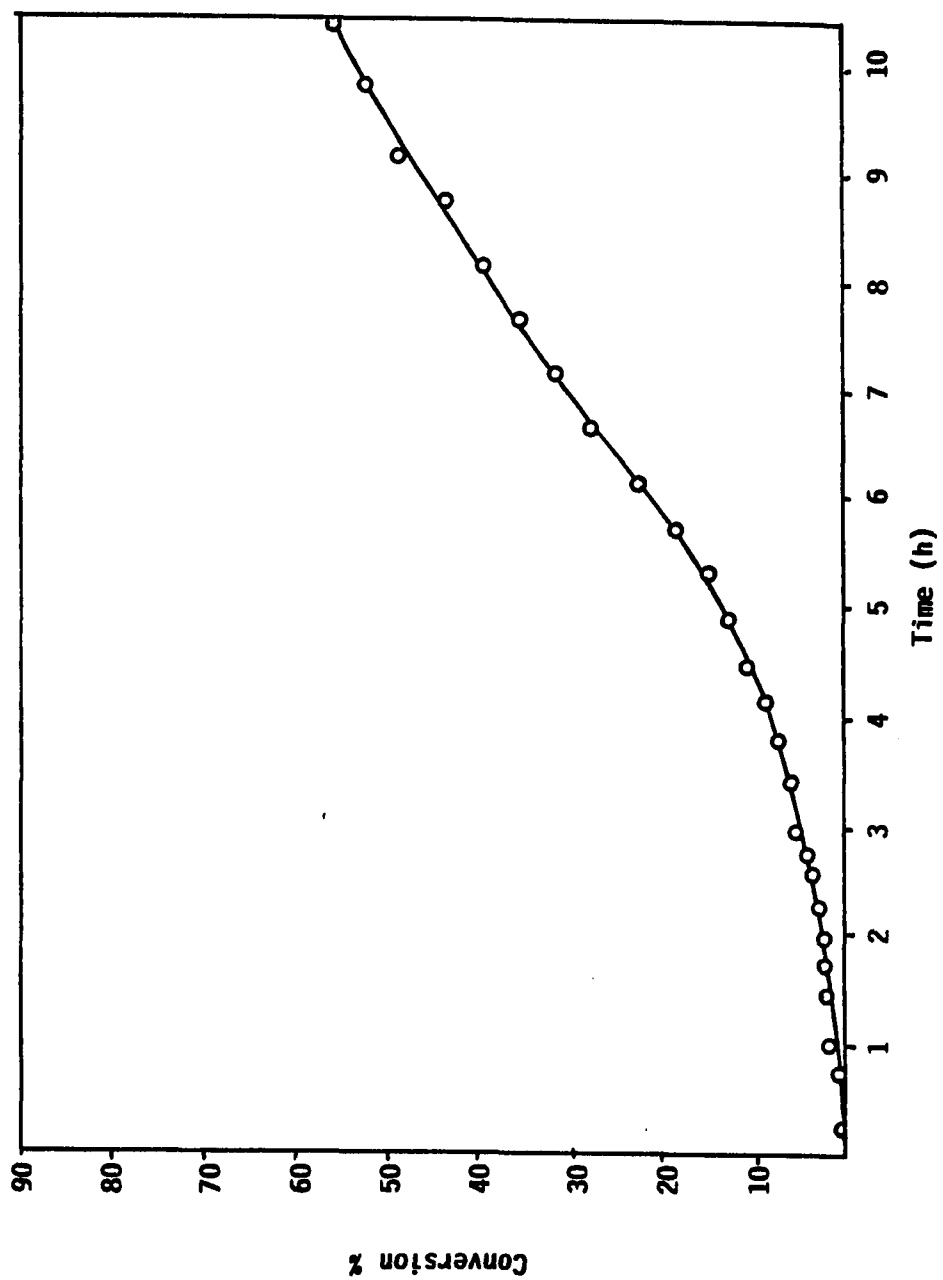


Figure D-4. Conversion vs. Time Plot of Recipe 66.

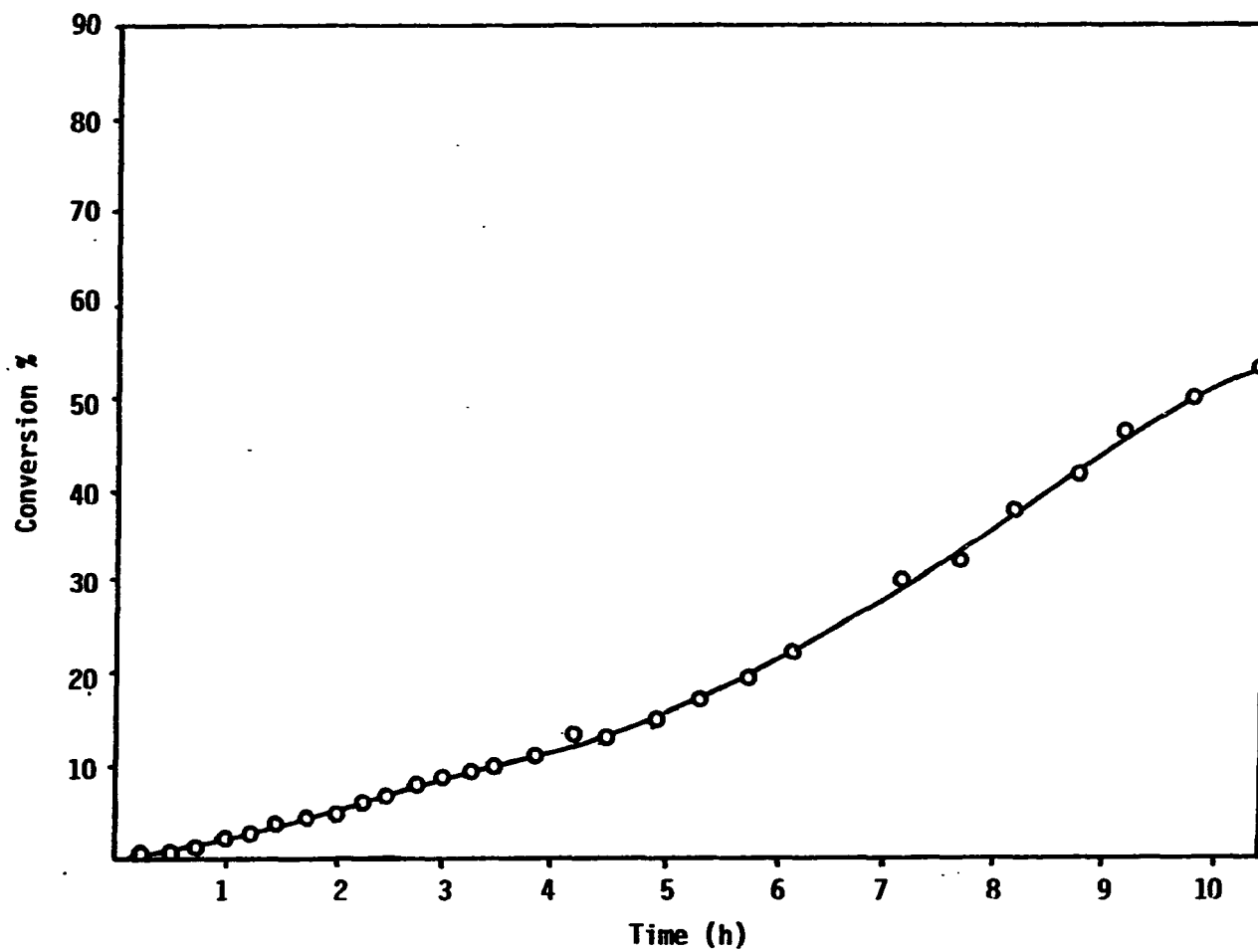


Figure D-5. Conversion vs. Time Plot of Recipe 67, with Increased Emulsifier Concentration.

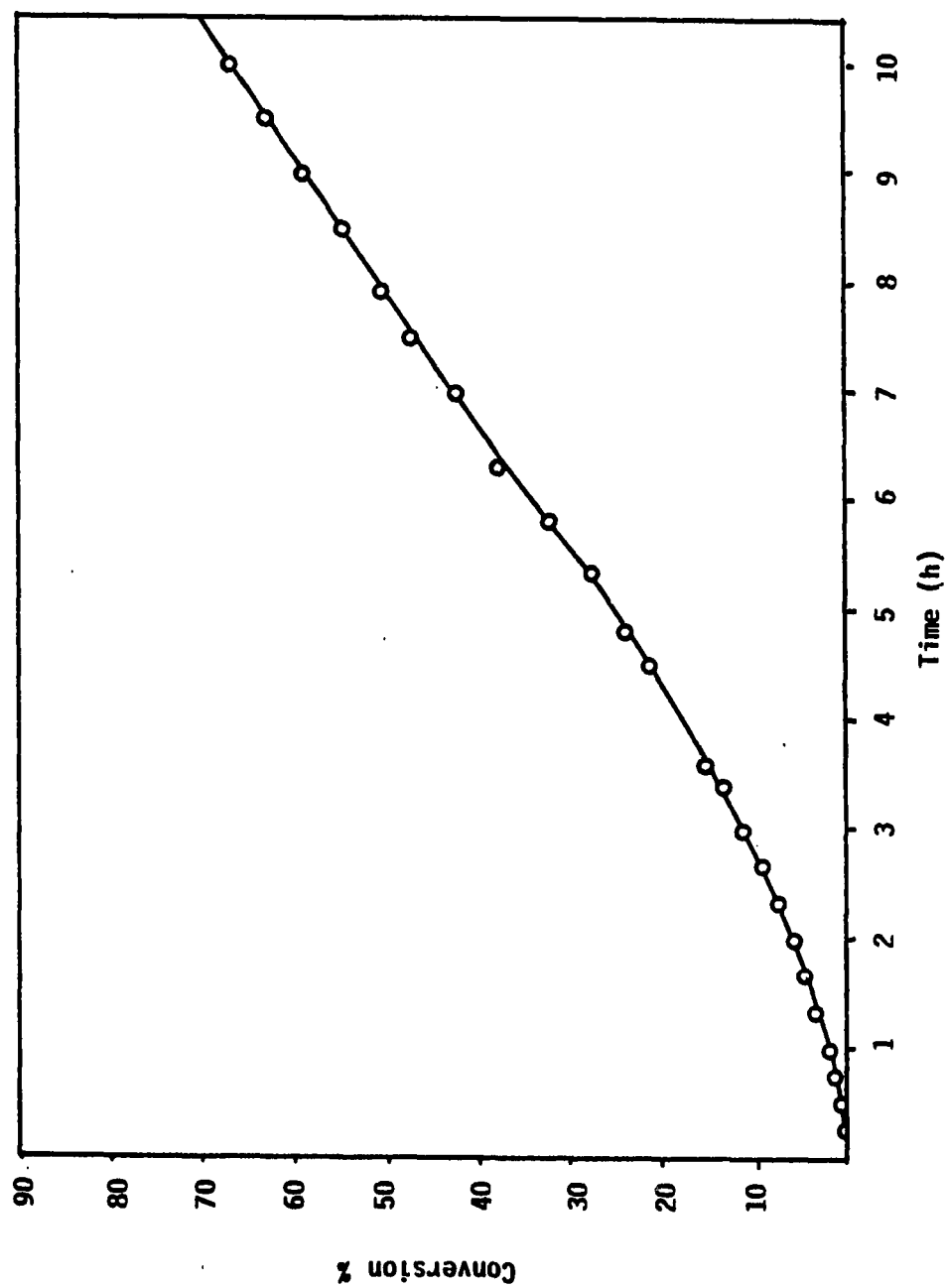


Figure D-6. Conversion vs. Time Plot of Recipe 67, with Increased Emulsifier Concentration.

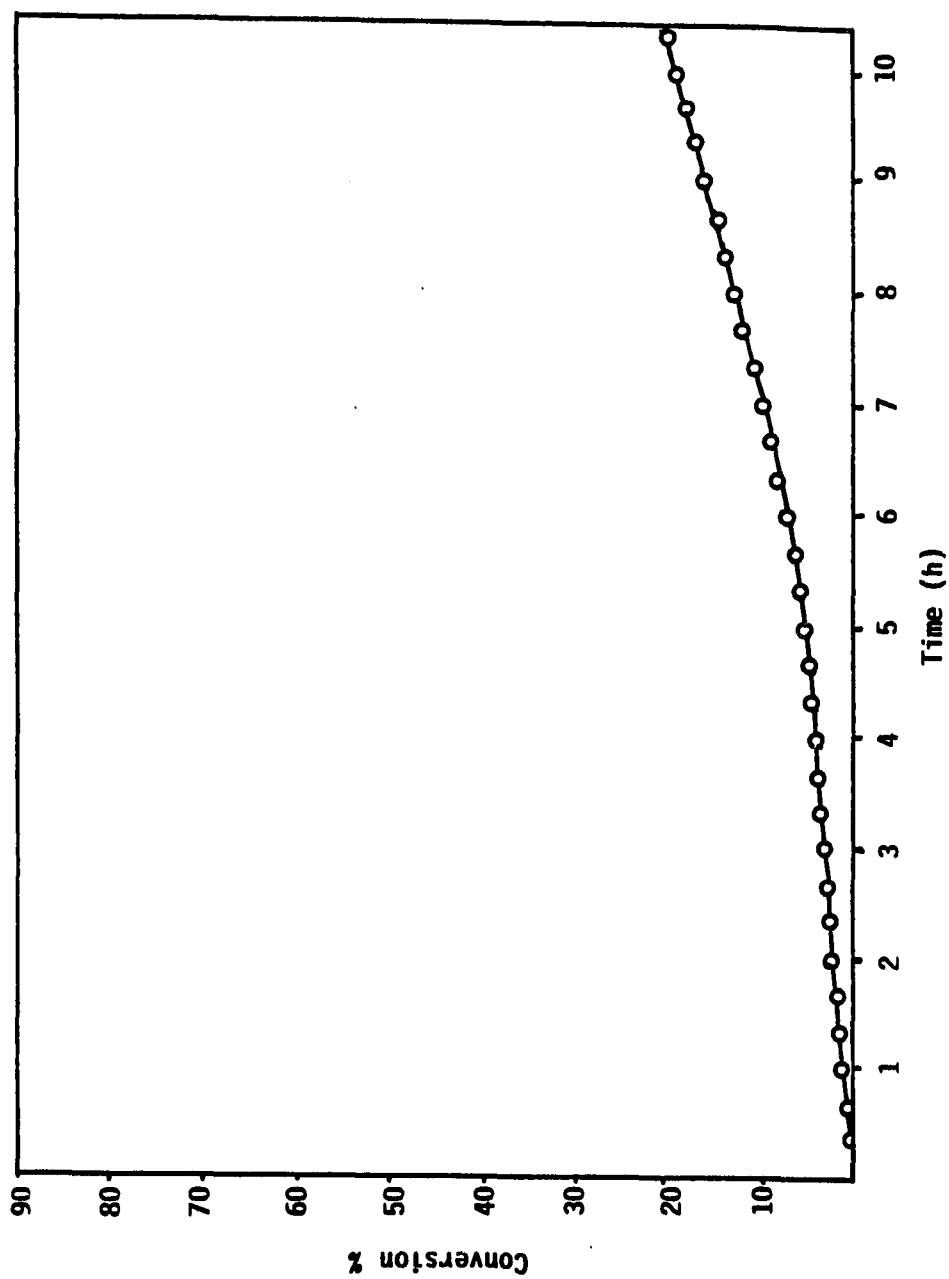


Figure D-7. Conversion vs. Time Plot of Recipe 68, with Decreased Initiator Concentration.

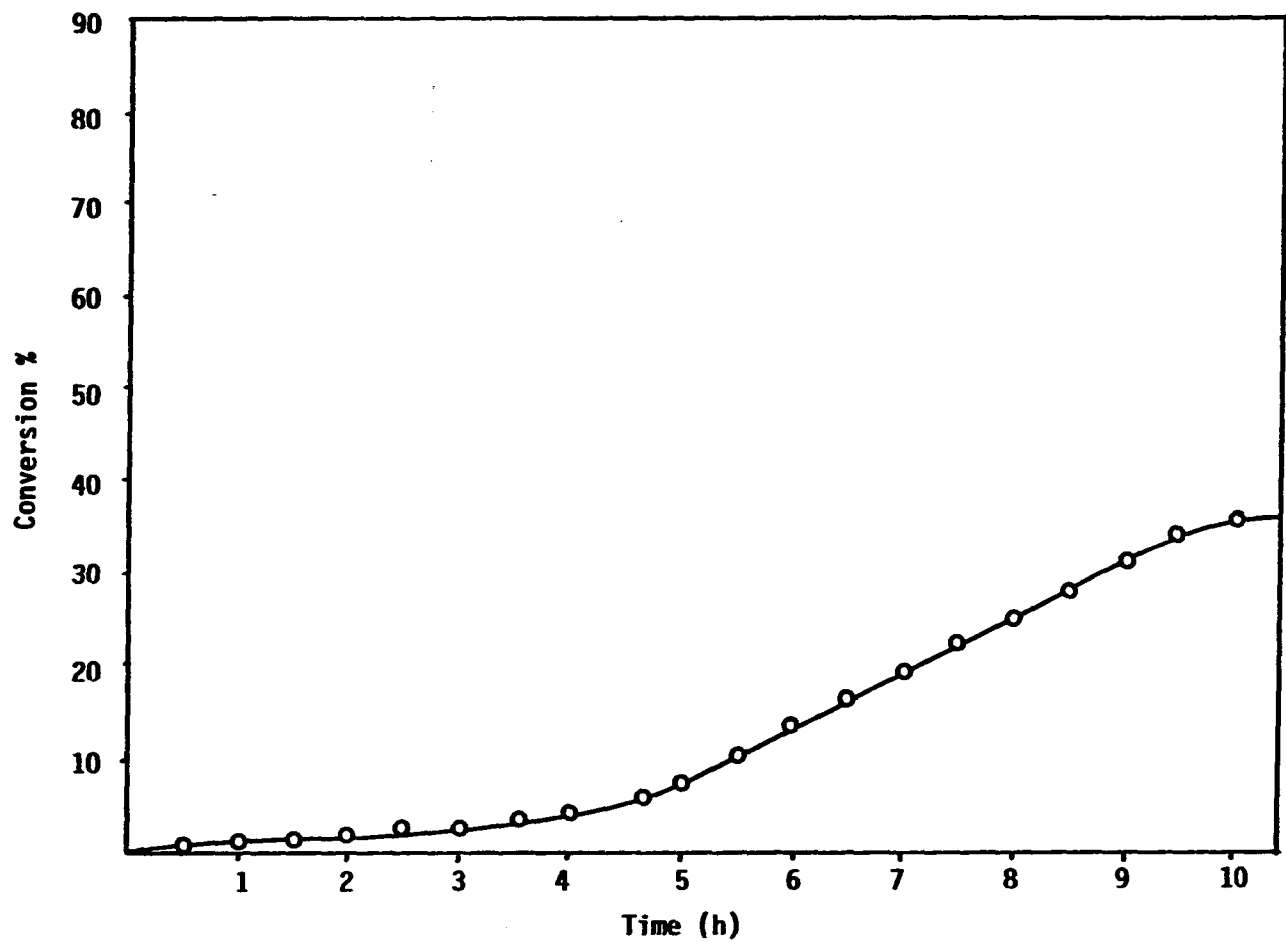


Figure D-8. Conversion vs. Time Plot of Recipe 68, with Decreased Initiator Concentration.

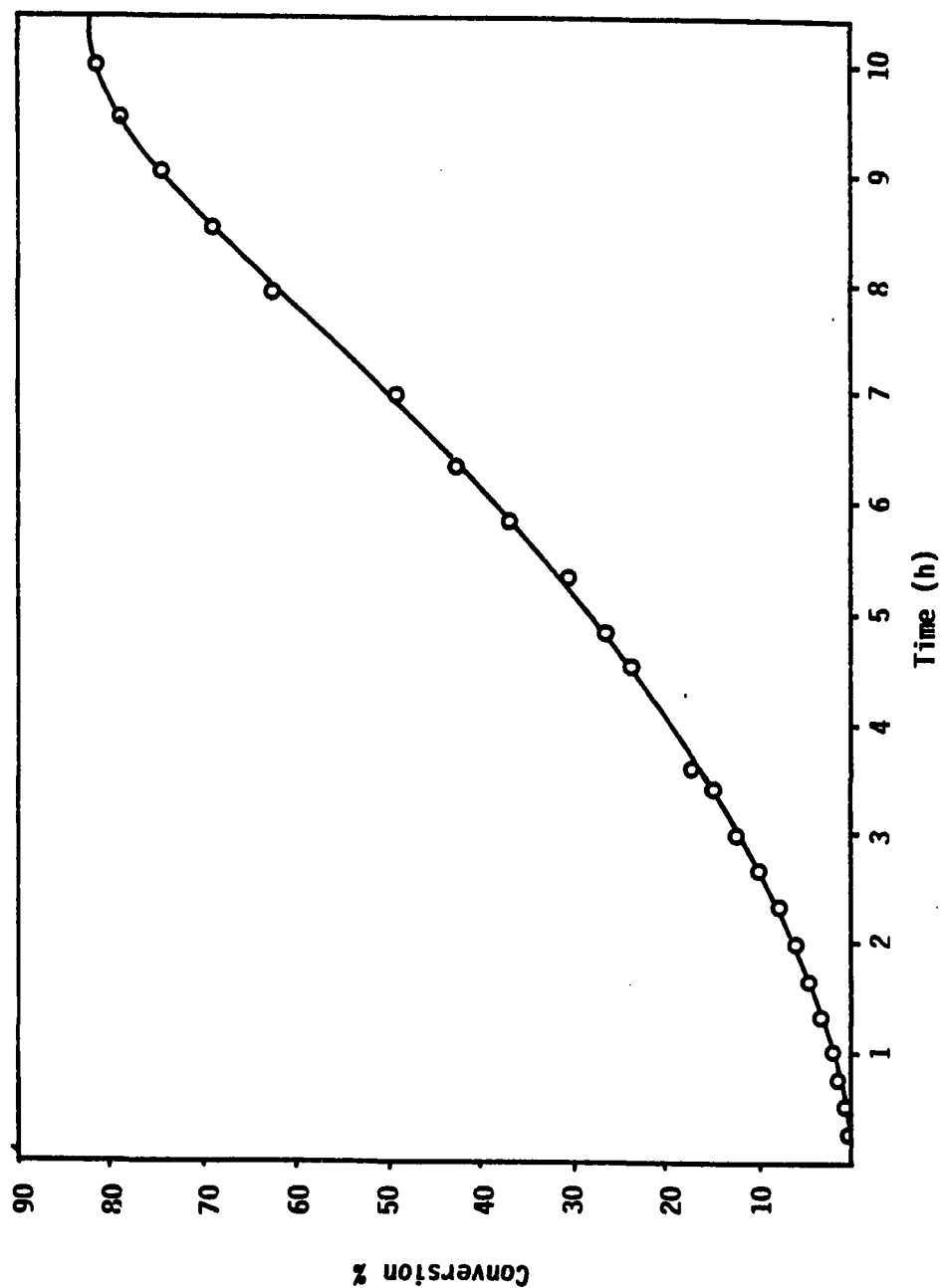


Figure D-9. Conversion vs. Time Plot of Recipe 70, with Increased Initiator Concentration.

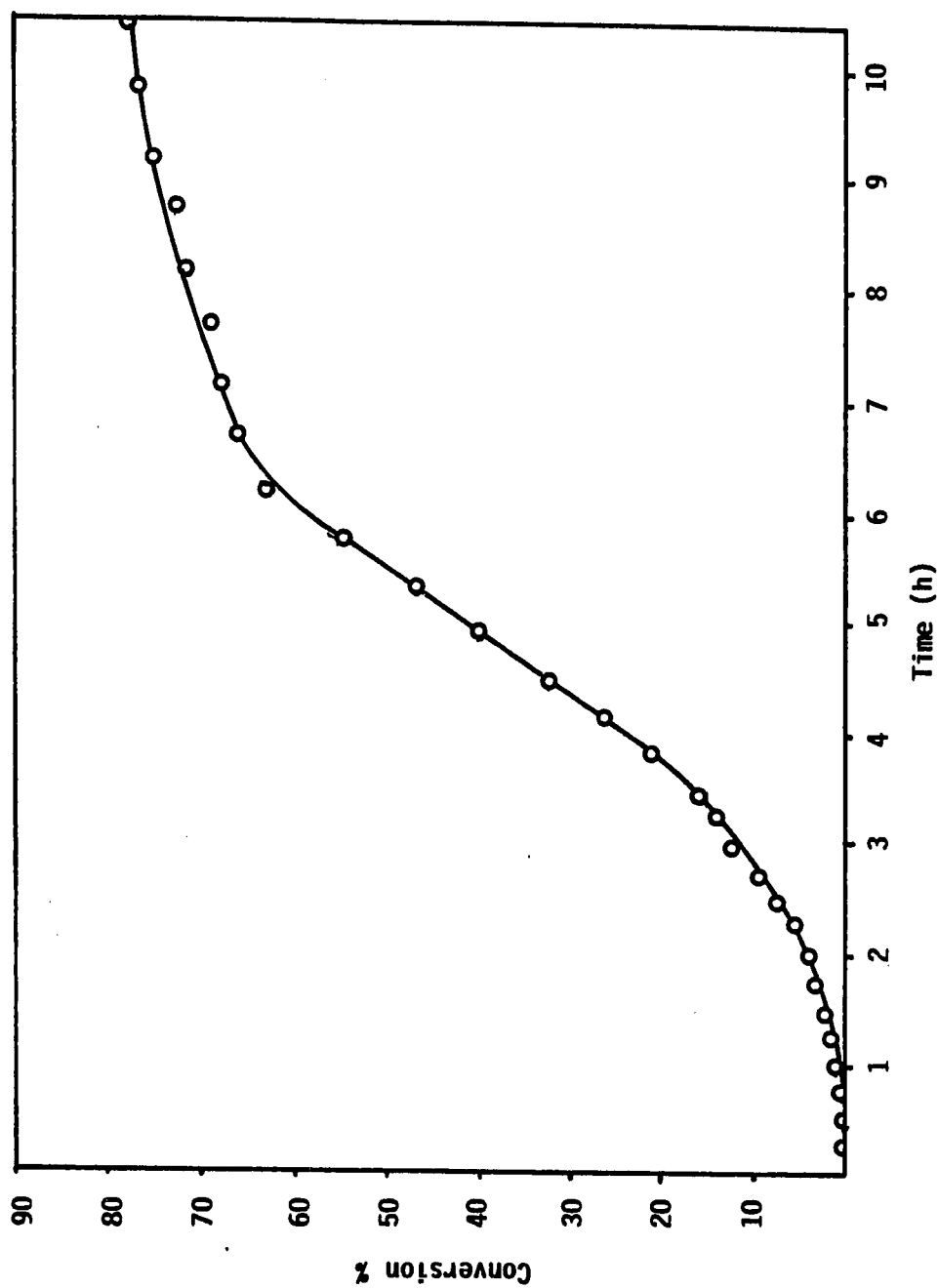


Figure D-10. Conversion vs. Time Plot of Recipe 70, with Increased Initiator Conversion.

REFERENCES

1. Ham, G. E., Ringwald, E. L. Crosslinking in Polymerization of Vinyl Benzoate and Related Compounds. J. Polym. Sci., 1951, 8, 91-93.
2. Merker, R. L., Scott, M. J. The Reaction of Alkyl Halides with Carboxylic Acids and Phenols in the Presence of Tertiary Amines. J. Org. Chem., 1960, 26, 5180-5182.
3. Berlin, K. D., Gower, L. H., White, J. W., Gibbs, D. E., Sturm, G. P. Synthesis and Structure Determination of Triethyl Esters. J. Org. Chem., 1962, 27, 3595-3597.
4. Hennion, G. F., Nieuwland, J. A. The Addition of Some Organic Acids to Alkyl Acetylenes. J. Am. Chem. Soc., 1934, 56, 1802-1803.
5. Adelman, R. E. The Interchange Reaction of Vinyl Acetate with Organic Acids. J. Org. Chem., 1949, 14, 1057-1077.
6. Hermann, O. W., Haehnel, W. Process of Preparing Vinyl Esters. U.S. Patent 2,245,131; June 10, 1941.
7. Toussaint, J. W., Mac Dowell, L. G. Preparation of Vinyl Esters. U.S. Patent 2,299,862; October 27, 1942.
8. Fumuaki, K., Tanaka, S., Honma, Y. Alkenyl Esters of Carboxylic Acids. U.S. Patent 4,425,277; January 10, 1984.
9. McKeon, J. E., Fitton, P. The Palladium(II) Catalyzed Vinyl Interchange Reaction. Tetrahedron, 1972, 28, 233-238.
10. Padney, N. R., Henry, P. M. Palladium(II) Catalyzed Exchange Reactions. Vinyl Propionate Exchange with Acetic Acid Catalyzed by Palladium(II) Acetate. Canadian J. Chem., 1975, 53, 2223-2231.
11. Rostovskii, B. Vinyl Benzoate Synthesis Using Zinc Acetate. Zhur. Priklad. Khim., 1954, 27, 2223-2225.
12. Fischer, H., Frytag, L. Vinyl Benzoate Synthesis Using Salts of Group I and II Metals. German Patent 740 987; May 12, 1946.
13. Lussi, H. Vinyl Benzoate Synthesis. Kunststoffe-Plast., 1956, 3, 156-160.

14. Heinman, H. K., Schmidt, H. Vinyl Benzoate Synthesis Using Cadmium Acetate. German Patent 1,134,665; September 15, 1962.
15. Bovey, F. A., Kolthoff, I. M., Medalia, A. I., Meehan, E. J. Emulsion Polymerization Vol IX. New York: Interscience Publishers, Inc., 1955, p. 15, 59, 141, and 271.
16. Jenkins, A. D., Ledwith, A. Reactivity, Mechanism and Structure in Polymer Chemistry. London: John Wiley and Sons, 1974, p. 175.
17. Odion, G. Principles of Polymerization, 2nd Ed. New York: John Wiley and Sons, 1984, p. 319.
18. Pirma, I., Gordon, L. J. Emulsion Polymerization. Philadelphia: ACS Symposium Series 24, 1975, p. 34.
19. Ham, E. G., Ringwald, E. L. Crosslinking in Polymerization of Vinyl Benzoate and Related Compounds. J. Polym. Sci., 1951, 8, 93-99.
20. Morrison, E. D., Gleason, E. H., Stannett, V. The Polymerization of Vinyl Benzoate. Inhibition by Monomer. J. Polym. Sci., 1959, 36, 267-273.
21. Burnett, G. M., Wright, N. W. The Polymerization of Vinyl Benzoate and Vinyl Propionate. Trans Faraday. Soc., 1953, 49, 1108-1113.
22. Santee, G. F., Marchessault, R. H., Clark, H. G., Kearny, J. J., Stannett, V. Polymerization of Vinyl Benzoate. Makromol. Chem., 1964, 73, 177-187.
23. Banarjee, S., Muthana, M. S. Kinetics of Polymerization of Vinyl Benzoate. J. Polymer. Sci., 1959, 37, 469-483.
24. Smets, G., Hertoghe, A. Branching and Grafting Reactions on Polyvinyl Benzoate. Makromol. Chem., 1956, 17, 189-200.
25. Mortimer, G. A. Polymerization of Benzene. J. Am. Chem. Soc., 1961, 84, 4986-4987.
26. Kamachi, M. Reversible Donor-Acceptor Complex of Propagating Radicals. J. Am. Chem. Soc. Div. Polym. Chem., 1979, 20, 567-570.

27. Kamachi, M., Satoh, J., Liaw, D. J. Comment on Radical Polymerization Mechanism of Vinyl Benzoate. Polym. Bull., 1979, 1, 581-584.
28. Woods, M. E., Dodge, J. S., Krieger, J. M., Piece, P. E. Emulsion Polymerizations with Mixed Surfactants. J. Paint Tech., 1968, 40, 543-548.
29. Medvedev, S. S., Griskova, J. A., Zurikov, A. V. The Emulsion Polymerization of Styrene in the Presence of Nonionic Emulsifiers. J. Macromol. Sci-Chem., 1973, A-7(3), 715-736.
30. Harkins, W. D. The General Theory of the Mechanism of Emulsion Polymerization. J. Am. Chem. Soc., 1947, 69, 1428-1444.
31. Smith, W. K., Ewart, R. H. Kinetics of Emulsion Polymerization. J. Chem. Phys., 1948, 16, 592-599.
32. Kamath, V. The Role of Mixed Ionic and Nonionic Surfactants on the Rate of Emulsion Polymerizations. Ph.D. Dissertation, University of Akron, Akron, Ohio, 1973.
33. Wang, A. The Effects of Surfactants on Rates of Emulsion Polymerizations. M. S. Thesis, University of Akron, Akron, Ohio, 1973.
34. Imoto, M., Choe, S. Vinyl Polymerization. Decomposition of Sym-Substituted Benzoyl Peroxides in the Presence of Dimethyl Aniline. J. Polym. Sci., 1955, 15, 485-501.
35. Bovey, F. A., Kolthoff, I. M. Medalia, A. I., Meehan, E. J. Emulsion Polymerization, Vol. IX., New York: Interscience Publishers Inc., 1955, p. 86.
36. Timmermans, J. Physio-Chemical Constants of Pure Organic Compounds. New York: Elsevier Publishing Co., 1950, 361, 415-416.
37. Encyclopedia of Polymer Science. New York: John Wiley and Sons, 1971, 15, 698.
38. Lowry, G. G. Private Communications, 1987.
39. Seymour, R. B., Carraher, C. E. An Introduction to Polymer Chemistry. New York: Marcel and Dekker Inc., 1983, p. 54-81.
40. Lowry, G. G. Private Communications, 1987.

41. Small, P. A. Some Factors Affecting the Solubility of Polymers. J. Appl. Chem., 1953, 3, 71-80.
42. Erhan, S. Z. Effect of Polymerization Conversion on the Experimental Determination of Monomer Reactivity Ratios in Copolymerization. Ph.D. Dissertation, Western Michigan University, Kalamazoo, Michigan, 1967.