Formation of Large Monodisperse Copolymer Particles by Dispersion Polymerization

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ABSTRACT: Monodisperse copolymer particles consisting of styrene and *n*-butyl methacrylate have been prepared in the 1–10-μm size range. These particles were prepared by dispersion polymerization in ethanol–water media using a single steric stabilizer to prevent coalescence. Several comonomer ratios were investigated, and it was observed that narrow size distributions could be achieved in all cases with essentially complete incorporation of monomer at the feed composition. Differences in the polarity of the starting solvent composition could be estimated with the solubility parameter and were found to have a significant effect on final particle size. Changes in the polarity of the reaction medium with conversion of monomer to polymer was observed to broaden the particle size distribution.

Introduction

Dispersion polymerization has recently been the subject of renewed research activity following reports that large monodisperse particles can be prepared by use of this technique.[1–3] Several systems have been reported that permit the preparation of monodisperse polymer colloids in the 1–5-μm size range in both polar and nonpolar media.[4,5] Typically, the resulting particles are made by polymerization of a single monomer.

Dispersion polymerization depends on the homogeneous nucleation of particles from the reaction medium in a manner similar to the particle formation process in emulsion polymerization. Therefore, when nucleation occurs in a short period of time at the start of the reaction and little or no coalescence occurs, monodispersity is expected. This process differs from emulsion polymerization in several important elements, including the use of a polymeric steric stabilizer instead of surfactant and the presence of a single phase at the beginning of the polymerization in contrast to the multiple phases present during an emulsion polymerization. Once polymerization has begun, the polymer being formed precipitates to produce particles that are stabilized by a soluble polymer added to the mixture as a graft copolymer (or as its precursor). The reaction medium therefore is selected on the basis of not only its nonsolvent properties for the forming polymer but also its solubility properties for the stabilizer and its miscibility with the monomer.

Barrett has reported the preparation of monodisperse poly(methyl methacrylate) dispersions in hydrocarbon media with a diameter of 1 μm using a graft copolymer steric stabilizer.[6] Barrett has also written an excellent review on the subject of dispersion polymerization in organic media.[7] Almog and co-workers have prepared both styrene and methyl methacrylate polymer particles by this approach using reaction medium soluble polymers as steric stabilizers in conjunction with ionic surfactants.[1] The size of the resulting particles, as large as 5 μm, was shown to be dependent on the polarity of the reaction medium chosen and correlated well with the solubility parameters of the reagents. Our laboratories have more recently reported the preparation of monodisperse polystyrene particles in mixed-alcohol media to as large as 10 μm using only nonionic cellulosic polymers as steric stabilizer with no charged cosurfactant.[2,3] The size of the resulting particles was also shown to be dependent on the polarity of the reaction medium as well as the rate of polymer formation.

The choice of steric stabilizer depends very much on the reaction medium being used, and in polar systems the stabilizer can be either an ionizable polyelectrolyte or a nonionic polymer. Block copolymers have been used effectively as stabilizers in hydrocarbon media to produce polymer particles.[12] Particles prepared by dispersion polymerization using all these types of materials have been reported. Corner has described polystyrene particles produced in aqueous ethanol media using poly(acrylic acid) (PAA) as steric stabilizer.[5] The size of the resulting particles was found to be dependent on the molecular weight of the PAA as well as its concentration, and monodisperse polystyrene particles of up to 3 μm were reported.

Very few reports in the literature deal with particles prepared by copolymerization. This is probably due to the complex nature of comonomer mixtures where each new comonomer ratio must be treated as a new polymerization system. These comonomer systems are even more complicated if the comonomers polymerize at different rates or partition differently in the system once nucleation has taken place. This paper describes work done on the polymerization of styrene and *n*-butyl methacrylate in a water–ethanol medium with poly(acrylic acid) as steric stabilizer. The effect of the comonomer ratio and reaction medium composition on particle size is discussed and has been found to be related to the polarity of the reaction medium as present during the initial nucleation stages of the polymerization.

Experimental Section

All organic reagents were purchased from Aldrich and were used without further purification. The poly(acrylic acid), MW ~ 250 000, was obtained from Polyscience in a typical polymerization; ethanol (200 mL), deionized water (18 g), and poly(acrylic acid) (3.5 g) were heated to 68 °C until all the polymer stabilizer dissolved. Under N_2 atmosphere and constant stirring, the comonomer (24 mL of styrene/16 mL of *n*-butyl methacrylate) along with the initiator benzoyl peroxide (1.5 g) was added all at once. Polymerization was allowed to continue for 48 h until the monomer was consumed. Isolated particles could be obtained by freeze-drying from water after centrifugation to remove the reaction medium.

Characterization of the resulting particles consisted of measurement of copolymer composition by ^{1}H NMR in $CDCl_3$ with tetramethylsilane (TMS) as internal reference and molecular weight determination with a Waters GPC using tetrahydrofuran (THF) as solvent and ultra-μStyragel columns. The instrument was calibrated by using monodisperse polystyrene standards purchased from Pressure Chemical. Both RI and UV detectors were employed, and the calculation of molecular weights was carried out by using a standard curve based on these polystyrene

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Table I
Reaction Composition,[a] Initial Solubility Parameter, and Resulting Diameter of Particles Produced from a 3:2 Volume:Volume Mixture of Styrene–*n*-Butyl Methacrylate at the 15% Comonomer Concentration

sample	H_2O, vol %	EtOH vol %	comonomer vol %	init δ, (cal/cm^3)$^{1/2}$	particle diam,[b] μm
1-1	5.5	78.5	16	13.0	12.3, GSD = 1.28
1-2	6.3	78.1	15.6	13.1	13.5, GSD = 1.17
1-3	7.0	77.5	15.5	13.2	7.2, GSD = 1.09
1-4	7.7	76.9	15.4	13.4	6.2, GSD = 1.1
1-5	8.4	76.3	15.3	13.5	5.9, GSD = 1.28
1-6	9.0	75.8	15.2	13.6	5.3, GSD = 1.41
1-7	9.8	75.2	15.0	13.7	2.41, PD = 4
1-8	17.2	69.0	13.8	14.7	0.068, PD = 3
1-9	25.0	62.5	12.5	15.7	0.58, PD = 0

[a] 3.5 g of PAA and 1.5 g of BPO per 200 mL of EtOH. [b] GSD, geometric standard deviation from Coulter counter; PD, polydispersity index from Coulter nanosizer.

standards. Particle size was measured with a Reichert Zetopan optical microscope using calibrated photomicrographs or by means of a Coulter counter. The measurement of conversion as a function of time was made by using a Varian aerograph Model Series 2800 gas chromatograph using a 10 ft × $^1/_8$ in. SS column packed with 20% SE-30 on 80/100 Chromosorb W with 5% dimethylchlorosilane (DMCS). For more detailed procedures of the synthesis and characterization of these types of materials, refer to ref 2 and 3.

Results and Discussion

The polymerization system under investigation consisted of styrene (S) and *n*-butyl methacrylate (BMA) comonomers, with ethanol and water as solvents. The stabilizer and initiator were poly(acrylic acid) and benzoyl peroxide, respectively. Under the correct reaction conditions, it was possible to prepare monodisperse copolymer particles with these materials. The role of the poly(acrylic acid) stabilizer was to prevent coalescence or aggregation of the growing particles, and this polymer has previously been used effectively with polystyrene and poly(methyl methacrylate) systems.[5]

A. Styrene *n*-Butyl Methacrylate Comonomer Mixtures. The first comonomer ratio to be studied was a 3:2 volume mixture of styrene and *n*-butyl methacrylate. Listed in Table I are the reaction conditions, reaction times to complete conversion, and the size of the resulting particles. Only the quantity of water added to the reaction mixture differed between the reactions listed: all other reagent concentrations were held constant. The change in the concentrations of water used would be expected to alter not only the polarity of the reaction mixture but also the partitioning properties of the reaction mixture. As can be readily observed, slight increases in the amount of water present caused incremental reductions in the particle size. In the range of reagent concentrations between 7.0 and 7.7 vol % water, monodisperse particles were produced, but outside this narrow range the size changed and the distribution broadened.

Those reaction compositions tested appear in Figure 1, a ternary phase diagram showing the initial reaction mixture composition of the 3:2 styrene–*n*-butyl methacrylate mixtures. The percentages of water, ethanol, and monomer in the starting mixture are plotted as a function of the total volume. Reactions carried out at 15% comonomer concentrations are represented here by circles; other data relating to this curve can be found in Table I. The two comonomers have been treated as a single species, since they copolymerize in their starting ratio. This would be expected on the basis of both their reactivity ratios[4] and the experimentally determined consumption of monomer shown in Figure 2. Note also in Figure 1 the possible reagent ratios that have been excluded. All regions with less than 10% monomer were not investigated, and a second boundary, indicated by the triangles linked with a solid line, marks the limit to single-phase behavior. Dispersion polymerization must occur within the region bounded by the cloud-point curve. Both of these boundaries are also shown in Figure 5, a plot of the 7:3 styrene–*n*-butyl methacrylate reaction conditions, but are slightly different due to the changed comonomer ratio.

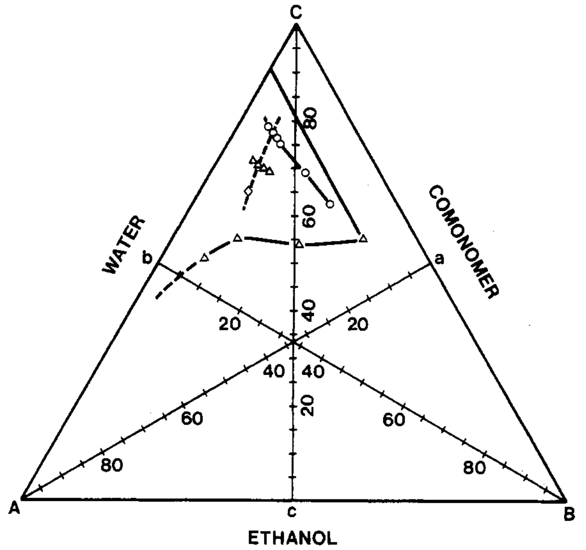

Figure 1. Ternary phase diagram of reactions made with 3:2 styrene–*n*-butyl methacrylate comonomer mixture.

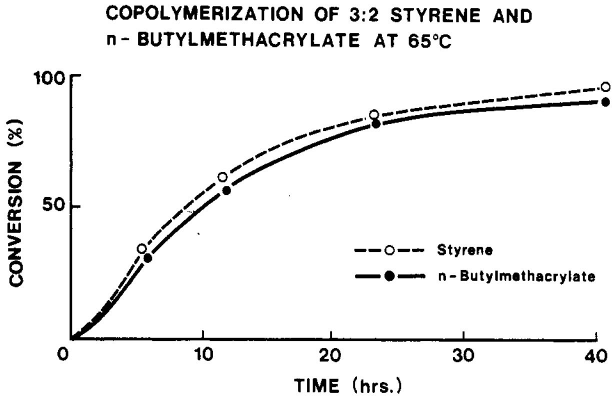

Figure 2. Plot of conversion of 3:2 styrene–*n*-butyl methacrylate vs. time.

A second series of runs at 20% comonomer, respresented by triangles, was also performed with increasing amounts of water. The difference between these conditions and those described above is that a 50% increase in the concentration of comonomer mixture was used as outlined in Table II. As can be seen from the results, it was again possible to prepare particles of the same size given the correct reagent mixture, but it required an increased amount of water, the more polar component, to reach this window. The single data points at 25% comonomer, shown with a diamond, will be discussed later in this report. The dashed line running through the three comonomer concentration studies is a curve representing the same polarity in the starting reaction mixture and is also discussed later.

Compositions with greater and lesser amounts of styrene than those described above were used to prepare other particles with similar sizes and narrow size distributions. Their ratios ranged from 1:1 to 4:1 styrene–BMA volume

Table II
Reaction Composition, Initial Solvency, and Resulting Particle Diameter of 3:2 Volume:Volume Mixture of Styrene-*n*-Butyl Methacrylate above 20% Comonomer Concentrations

sample	H_2O, vol %	EtOH, vol %	comonomer, vol %	init δ, (cal/cm^3)$^{1/2}$	particle diam,[a] μm
2-1	6.5	71.9	21.6	13.0	3–20
2-2	7.8	70.9	21.3	13.2	8.2, GSD = 1.2
2-3	8.8	70.2	21.2	13.3	1–8
2-4	10.3	69.0	20.7	13.6	0.5–2
2-5	9.1	64.9	26.0	13.2	4.7, GSD = 1.6

[a] GSD, geometric standard deviation.

mixtures; Table III contains the data observed for these other compositions. It was possible to determine combinations of monomers and solvents necessary to produce copolymer particles of roughly 7 μm in diameter with a narrow size distribution for all comonomer ratios. These materials were analyzed for their composition, molecular weight, and size as reported in Table IV.

The composition of these particles was determined by ^{1}H NMR and, within experimental error, there were no differences between the expected and the experimentally measured values. The molecular weight of all copolymer materials was approximately 12×10^3 (M_n) and 26×10^3 (M_w) based on polystyrene standards. Except for the 1:1 comonomer sample that gave smaller particles and a wider distribution, the sizes of all the copolymer spheres were in the same size range and had quite narrow size distributions. It should be evident therefore that subtle changes in reaction conditions and monomer ratio can be used to alter the size and size distribution of these materials in a systematic and well-controlled manner.

B. Effect of Initial Medium Polarity. Two features of size control are evident from the data presented in Tables I–IV. As comonomer formed an increasingly greater proportion of the reaction mixture, it was necessary to increase the amount of water present in order to prevent an increase in the final particle size. Further, as the amount of *n*-butyl methacrylate was increased with respect to the quantity of styrene present, an increase in the fraction of water present was required to maintain the same particle size. Both effects demonstrate the influence that the polarity of the medium during the particle nucleation stage had on the ultimate particle size and distribution.

One method of estimating the polarity of a mixture of miscible liquids involves averaging the solubility parameter of the components.[9] The solubility parameter, δ, is an empirical quantity that permits the calculation of a value representing the polarity of a solvent medium.

The calculation of δ for a solvent mixture is done by taking the average based on the volume fraction of solvent in the mixture.[10] The average used in the calculations reported here is given by

$$\delta = (\sum \Phi_i \delta_i^2)^{1/2}$$

where Φ_i is the volume fraction of component i. A numerical value for solution δ could be determined on the basis of the relative composition of the low molecular weight materials in a manner similar to that reported earlier.[10] The single component solubility parameter was chosen in favor of other more accurate methods because of the availability of values for all reaction components considered in this report. Neither the polymeric stabilizer nor intiator was used in these estimations since they were present in small quantities. The polymer produced from the monomer was not included in the calculations since it was located in a separate phase. One of the limitations of this method for estimating the solubility parameter is that the effect of the polyelectrolyte nature of poly(acrylic acid) is completely ignored. Slight changes in ionization could drastically alter the solubility parameter of the system even in low concentrations. In view of the fact that poly(acrylic acid) has been substituted with nonionic stabilizers such as (hydroxypropyl)cellulose and poly(vinylbutyral) to obtain similar results it is believed that the ionic nature of the PAA in the alcoholic media is minimal.[13] The temperature, if changed, would be expected to affect

Table III
Reaction Composition and Particle Diameters for Various Comonomer Ratios

sample	H_2O, vol %	EtOH, vol %	comonomer vol %	comonomer ratio (S/B)[a]	particle diam or range,[b] μm	init δ, (cal/cm^3)$^{1/2}$
3-1	4.0	80.0	16.0	7/3	1–15	12.8
3-2	4.8	79.4	15.9	7/3	9.0 (1.1)	12.9
3-3	5.9	78.4	15.7	7/3	4–7	13.1
3-4	7.0	77.5	15.5	7/3	1–5	13.3
3-5	6.9	66.5	26.6	7/3	6.6 (1.2)	12.9
3-6	2.4	81.3	16.3	4/1	2–10	12.6
3-7	3.2	80.6	16.1	4/1	6.5 (1.2)	12.7
3-8	4.0	80.0	16.0	4/1	2–7	12.8
3-9	4.8	79.4	15.9	4/1	1–3	12.9
3-10	9.4	75.5	15.1	1/1	3.8 (2.1)	13.6

[a] S/B represents volume ratio of styrene to *n*-butyl methacrylate. [b] Number in parentheses is the geometric standard deviation measured by Coulter counter.

Table IV
Molecular Weight and Diameter for Particles Produced with Various Comonomer Ratios

sample	comonomer vol ratio, (S/B)	calcd comp, mol % S	exptl comp, mol % S	M_n ($\times 10^3$)	M_w ($\times 10^3$)	diam,[a] μm	init δ, (cal/cm^3)$^{1/2}$
4-1	1/1	60.0	60.0	13.2	28.8	3.8 (2.05)	13.6
4-2	3/2	68.0	69.9	11.5	24.1	7.2 (1.09)	13.2
4-3	7/3	77.0	76.0	11.2	25.4	9.0 (1.11)	12.9
4-4	4/1	83.5	84.7	14.6	29.6	6.5 (1.18)	12.7
4-5	1/0	100	100	11.4	20.7	9.1 (1.09)	11.5

[a] Number in parentheses is the geometric standard deviation measured by Coulter counter. [b] Sample prepared in Methyl Cellosolve–ethanol (ref 3).

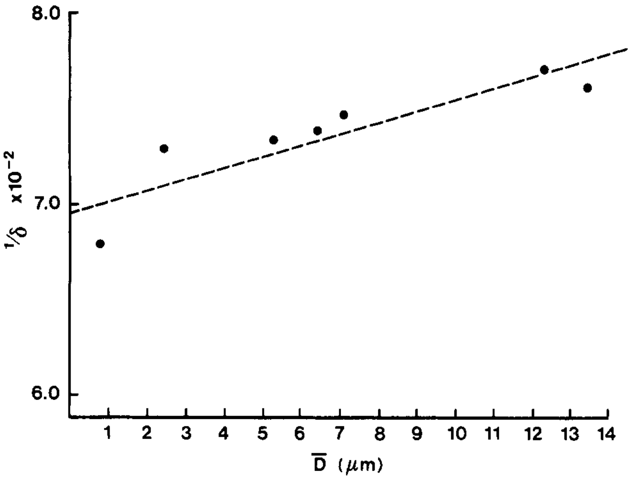

Figure 3. Plot of reciprocal solubility parameter vs. particle diameter.

the thermodynamic properties of the reaction medium. It is clear from our earlier studies that the particle formation process involves a fractionation mechanism, and this is closely tied to the solubility of the polymer as a function of the polymer molecular weight.[3] The Θ temperature, the temperature at which the second virial coefficient is zero, is related to the difference between the solubility parameters of the polymer and solvent medium. The Θ temperature is dependent on the molecular weight of the polymer at low degrees of conversion, and so a 10-deg change of temperature can be shown to affect the solubility of such low molecular weight species.[11] In the same way, the solubility of the steric stabilizer can be influenced by reaction temperature and make the stabilizer either a better or worse stabilizer to an unknown degree.

Related to the temperature dependence of the polymer solubility, a molecular weight dependence also exists: the higher the polymer molecular weight, therefore, the lower the polymer solubility. This and other factors are functioning to cause nucleation of the polymer. All polymerization reactions in these studies were carried out at identical temperatures, so, while temperature was an important factor in polymer solubility, comparisons of the other factors could be made.

The initial solubility parameters for the reaction mixtures reported in Table I were calculated and are also given in the same table. Clearly, some form of inverse relationship can be observed between the final particle diameter and the initial polarity, and when the data are plotted in this manner as in Figure 3, there exists a straight line relationship. A similar trend was mentioned by Barrett,[7] but in another interesting series of experiments Almog and co-workers noted instead a dependence of the particle volume on the difference between the reaction mixture solubility parameter and that of the polymer, $\delta_{\mathrm{mix}} - \delta_{\mathrm{p}}$.[1] Whatever the precise form of the relationship, there is a decrease in the particle size with increased polarity of the reaction medium when nonpolar monomers are polymerized in polar media.

An increase in the initial comonomer concentration at fixed comonomer ratio required a simultaneous increase in water concentration; however, when the data for reaction 1-3 (15% monomer, Table I) were compared with that of reaction 2-2 (20% monomer, Table II), it was observed that δ was in both cases 13.2. To test the predictive power of these observations, a mixture with 25% 3:2 styrene–n-butyl methacrylate (reaction 2-5) was polymerized. Reagent conditions were such that δ was again 13.2, and, in fact, particles of approximately the same size were produced with a broadening of the size distribution.

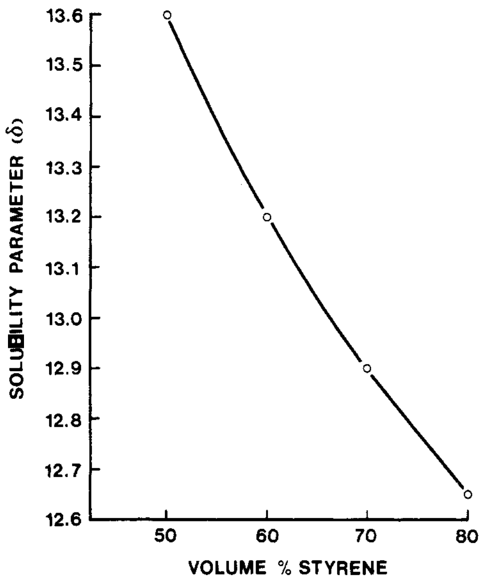

Figure 4. Plot of solubility parameter (δ) of monodisperse particle producing reactions vs. vol % styrene in comonomer mixtures.

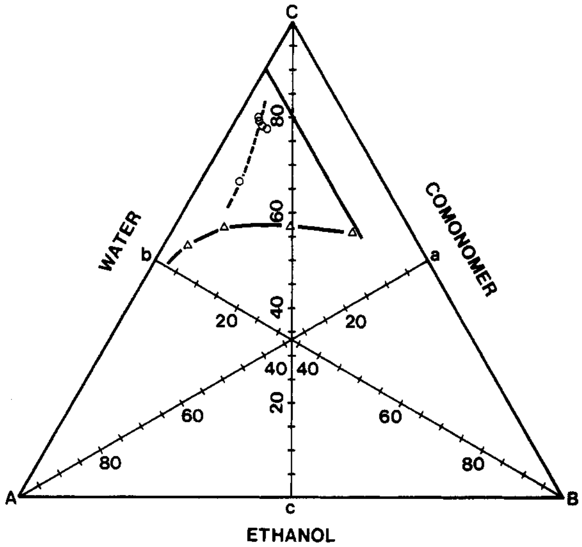

Figure 5. Ternary phase diagram of reactions made with 7:3 styrene–n-butyl methacrylate comonomer mixtures.

Further tests of this polarity rationale included the polymerization of 7:3 comonomer mixtures (Table III) at 25% comonomer concentrations (reaction 3-5), which could be compared with reaction 3-2 having 15% comonomer. In both cases the calculated δ was 12.9, and both reactions produced particles of effectively the same size. Figures 1 and 5 show plots of reaction mixture composition for the 3:2 and 7:3 comonomer mixtures, respectively. The dashed curve in both plots was a line of constant polarity, and as long as the initial reaction conditions fell in the region of this curve, particles of the same size were produced. As will be discussed below, reaction compositions with higher monomer concentrations gave broader distributions.

The other data shown in Table III for 4:1 and 7:3 comonomer ratios produced the same overall trends. Data for which only the range is shown had an average particle diameter in the middle of this range. Also given in Table III is the result of a single experiment using a 1:1 styrene–n-butyl methacrylate ratio. At this reaction composition, only 3.8-μm particles were produced. Lower polarity reaction mixtures (δ < 13.6) are therefore needed to produce larger particles.

Table V
Reaction Composition, Particle Size, Initial Solvency and Solvency Change of Selected Polymerizations[a]

sample	monomer (ϕ_1 = 0.15)	ethanol (ϕ_2)	solvent II (ϕ_3)	D, μm	δ_i, (cal/cm^3)$^{1/2}$	$\delta_i - \delta_f$, (cal/cm^3)$^{1/2}$
5-1	1:1 S–B	0.09	H_2O (0.76)	3.8	13.6	0.6
5-2	3:2 S–B	0.07	H_2O (0.78)	7.2	13.2	0.6
5-3	7:3 S–B	0.05	H_2O (0.79)	9.0	12.9	0.6
5-4	4:1 S–B	0.03	H_2O (0.81)	6.5	12.7	0.6
5-5[b]	S	0.60	MeCell (0.25)	2.7	11.9	0.3
5-6[b]	S	0.43	MeCell (0.43)	6.2	11.7	0.4
5-7[b]	S	0.30	MeCell (0.55)	9.1	11.5	0.4
5-8[b]	S	0.63	DME (0.22)	9	11.4	0.4
5-9[b]	S	0.43	Cell (0.43)	8	11.3	0.3
5-10[b]	S	0.70	THF (0.15)	9	11.7	0.4
5-11[b]	S (0.3)	0.7		5.5	11.8	1.2

[a] Abbreviations in table: S, styrene; B, *n*-butyl methacrylate; MeCell, 2-methoxyethanol; DME, dimethoxyethane; Cell, 2-ethoxyethanol; and THF, tetrahydrofuran. [b] Calculated from data previously reported in ref 3.

As the relative amount of styrene increased in the comonomer mixture, a decreasingly polar (or lower δ) reaction mixture was required to give $\sim$7-μm particles. The solubility parameters of monodisperse particle producing reaction mixtures given in Table IV have been plotted as a function of copolymer composition in Figure 4, and there the monotonic decrease in required δ with increased styrene comonomer fraction is apparent. This is not unexpected since the copolymer becomes increasingly soluble in ethanol–water with increasing concentrations of *n*-butyl methacrylate. Therefore, greater quantities of water, the most polar component in the reaction mixture, are required to cause precipitation of newly formed polymer, thereby creating particle nuclei. Molecular weights of the polymer were all in the same range, and compositions of the starting mixture matched those of the resulting polymer.

Appearing in Table V are the compositions of the different copolymerization mixtures that gave monodisperse particles. For comparison, reaction mixtures appearing in an earlier report giving polystyrene particles are also included.[3] These compositions are listed in turn with δ values of the initial and final reaction mixture calculated with the following solubility parameters: water (23.4), ethanol (12.7), Methyl Cellosolve (11.4), Cellosolve (10.4), styrene (9.3), THF (9.3), *n*-butyl methacrylate (8.3), and dimethoxyethane (8.3).[8]

It was determined that the δ_i of the reaction system for producing 6-μm polystyrene particles was 11.7 when ethanol–Methyl Cellosolve was used at 15% monomer concentrations (reaction 5-6). Calculations of the solvent system required for synthesis of particles of the same size at 30% monomer revealed that only ethanol was needed as solvent (reaction 5-11). The test reaction under these conditions produced particles of the same approximate size and further confirmed that initial solvent polarity was important in determining particle size.

Reaction systems producing particles of about 10 μm were obtained (reactions 5-8 to 5-10) by using various cosolvents in addition to ethanol.[3] The solubility parameters were all in the range of 11.5, the same as for Methyl Cellosolve–ethanol, but broad distributions were obtained. The correct polarity alone is therefore not sufficient to produce monodisperse particles, and the polymerization must also depend on the interaction of the solvent and stabilizer. An estimation of the solvent polarity will not consider the possibility of side reactions to either solvent or stabilizer or even chain transfer to initiator. Side reactions and chain transfer can reduce the molecular weight of the polymer being formed and thereby alter the particle nucleation and growth mechanism. Insufficient grafting or the absence of stabilizer will lead to very little stability of the growing particles and therefore rapid coalescence will take place. Many of the conclusions made in this report apply only to systems with sufficient concentrations of an effective stabilizer to inhibit coalescence. If coalescence occurs, induced by poor stabilization, then the trends described will not be evident.

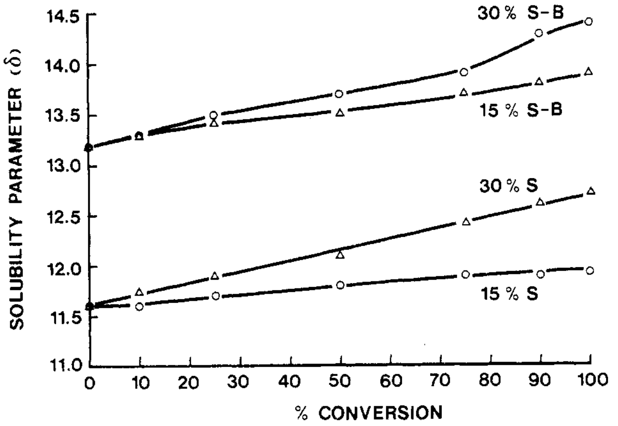

Figure 6. Solubility parameter plotted against conversion for styrene (S) homopolymerization and for 3:2 styrene–*n*-butyl methacrylate (S–B) copolymerization in 15% and 30% monomer reactions.

C. Changes of Polarity with Conversion. Measurement of the conversion permitted an estimation of the solubility parameter at any given time during the reaction since concentrations of all components contributing to δ were known. These calculations of δ were made for two reaction systems and were plotted against conversion in Figure 6. The final solubility parameter, δ_f, of most reactions was also calculated and was used to determine $\delta_f - \delta_i$. The difference between the final and initial solubility parameters is shown in Table V. Note that in almost all cases where monodispersity was achieved, $\Delta\delta$ was in the range of 0.7 or less. At higher concentration of monomer, the drift in δ is much greater with changing conversion.

The change in medium polarity is a very important parameter in determining the particle size distribution because, if the change is small, the nucleation conditions throughout the polymerization will be effectively constant. If the polarity change is large, nucleation conditions will change, and species that do not nucleate early in the reaction might do so later, resulting in a spread of particle size. This phenomenon has been observed when concentrations of monomer have been increased because the change in polarity is larger with higher starting concentrations of monomer as shown in Figure 6. With higher monomer concentrations, therefore, a broadening of the particle size distribution occurs. Clearly, a balance of the rate of initiation, polymerization, and precipitation must also be present in order to produce monodisperse particles. Such factors have been investigated for the polystyrene system and are reported elsewhere.[14]

Conclusions

The experimental conditions have been determined that enable the synthesis of styrene and *n*-butyl methacrylate copolymer particles possessing different relative compositions and essentially the same size and narrow size distribution. These studies have demonstrated the importance of the polarity of the polymerization mixture during the nucleation stage in determining the ultimate size of the copolymer particles. When the solubility parameter of the starting mixture known to give the desired particle size and distribution was employed, the necessary conditions could be estimated to produce the same particle size both at different monomer concentrations and in different solvent systems. A significant drift in the reaction mixture polarity has been found to broaden the distribution of the growing particles, and this has been explained in terms of the formation of nuclei later in the reaction. If such a drift in polarity did not occur, then the distribution would remain narrow in the absence of coalescence.

Registry No. (BMA)(S) (copolymer), 25767-47-9.

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Orientation Dynamics of Main-Chain Liquid Crystal Polymers. 1. Synthesis and Characterization of the Mesogen

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ABSTRACT: We have synthesized and characterized a family of liquid crystal copolyesters for a study of orientation kinetics described in the second paper of this series. The difference among members of this homologous series of main-chain liquid crystal polymers is molecular weight. Their backbones are formed by the condensation of pimelic acid and 4-acetoxyphenyl 4-acetoxybenzoate at temperatures in the range 180–285 °C. The polymers were characterized by ^{13}C and ^{1}H high-resolution NMR, differential scanning calorimetry, vapor pressure osmometry, optical microscopy, and solution viscometry. The NMR data indicate that random terpolymers are formed during the polymerization reaction, presumably as the result of transesterification of the central ester bond in the diacetoxy monomer. The family of random liquid crystal polymers synthesized covers the molecular weight range 3900–15 800. A major endotherm is observed for all molecular weights within 3 °C of 142 °C, and optical evidence for a nematic structure is definitely observed above 185 °C. An optically visible biphasic structure is not observed below 220 °C. Calculations using a chemical model designed from experimental data predict insignificant changes in polydispersity within the molecular weight range of the polymers studied. The detailed chemical characterization is critical to our understanding of liquid crystal microstructure and dynamics. This connection is discussed in the next paper of the series.

Introduction

The type of structural chemistry associated with thermotropic, main-chain liquid crystal polymers has been well established in previous work.[1–25] In contrast, many fundamental physical properties of these materials and their relationships to molecular variables have not been extensively studied. We cite here some papers in the literature addressing this topic.[26–32] Moreover, the organization of macromolecules in the liquid crystal phase and in solids derived from anisotropic melts remains unclear. Because of their inherent anisotropy and their ability to "freeze in" field-induced orientation, these polymers may prove useful in the development of materials that exhibit special properties such as nonlinear optical behavior, piezo- and pyroelectricity, and anisotropic conductivity as well as systems with information-storage capabilities. Studies on all aspects of structure vs. properties in liquid crystal polymers will undoubtedly be useful in the molecular design of these advanced materials. This series of papers presents our findings on some physical aspects of field-induced orientation in main-chain mesogens.

Elucidating relationships between molecular variables and physical properties requires synthesis and complete characterization of a suitable material. This has therefore been the topic addressed in the first paper of the series. Detailed characterization of chemical microstructure has posed a difficult problem for many liquid crystal polymers, owing to their insolubility in common, nondegrading solvents. Thus, the usual methods of structural elucidation such as high-resolution NMR are often not feasible. Also, many liquid crystal polymers possess nonregular sequences of structural units,[18–25] and it is therefore important to characterize their chemical microstructure. For example, Ober et al.[18] were able to show through carefully designed chemistry that the thermal transition behavior of liquid crystal polymers is quite sensitive to regioregularity. In fact, this study revealed that systems with purely alternating head-to-tail/tail-to-head sequences (syndioregic) had less of a tendency to form anisotropic phases than aregic materials. It was suggested that chemical defects

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