lines to infinite pitch ($1/P = 0$) suggests that the compensation temperature is below −50 °C for the left-handed samples and over the boiling point of chloroform for the right-handed samples. It is difficult to achieve these temperatures experimentally. However, if the trends shown in Figure 9 are maintained at intermediate acetyl contents, a thermally induced reversal of pitch is to be expected for long-pitch samples with acetyl contents near DA* at this concentration. So far, no temperature-induced reversal of handedness has been observed for any lyotropic or thermotropic liquid crystal derived from cellulose.[25]

Concluding Remarks

Cholesteric liquid crystal solutions of (acetyl)(ethyl)cellulose (AEC) in chloroform exhibit an unusual optical property, changing from a left-handed to a right-handed helicoidal structure with increasing acetyl content. The change occurs at a critical degree of acetylation, DA*, of around 0.18–0.20 for these AEC solutions. The acetyl content of AEC also strongly influences the magnitude of the cholesteric pitch and its temperature dependence. For acetyl contents below DA*, the cholesteric solutions are left-handed, with pitches which increase with acetyl content and decrease on heating. For acetyl contents above DA*, the solutions are right-handed, and the pitches decrease with increasing acetyl content and increase on heating. The significant dependence of chiroptical properties on apparently minor changes in acetyl content suggests that molecular properties influencing chain conformations may play a dominant role in governing the cholesteric properties of these cellulosic polymers. This inference is supported by the recent observation[26] that formation of trifluoroacetate esters on the cellulosic backbone cause a reversal of handedness for cellulose acetate mesophases in trifluoroacetic acid.

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Registry No. AEC, 37228-10-7; EC, 9004-57-3.

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Chain Propagation/Step Propagation Polymerization. 5. Telechelomer Polymerization via Alanine Mediation

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ABSTRACT: The polyesterification of a monodisperse poly(oxyethylene-*b*-pivalolactone) telechelomer, having M_n of 2700 and containing –OH and –COOH end groups, is described. Polymerizations were attempted with no success using selected (a) activating agents, (b) dehydrating agents, and (c) esterification catalysts, wherein the reactions were monitored by size-exclusion chromatography, viscometry, and nuclear magnetic resonance. Success was achieved with titanium tetrabutoxide catalysis in the presence of alanine to give high molecular weight polymers. A 5-fold increase in viscosity was observed as the alanine-mediated polyesterification progressed, and the $\bar{M}_{GPC}$ of the polymer obtained was 31 000. Reaction conditions could be optimized to avoid side reactions. The function of alanine in the esterification reaction is not yet clear; however, functions include (a) acting as a dehydrating agent, (b) acting as a template, and (c) increasing the effectiveness of titanium tetrabutoxide catalyst.

Introduction

Research in the field of multiphase segmented copolymers, although some 30 years old, remains quite active,[1,2] in part due to the wide range of physical behavior exhibited by these copolymers, ranging from impact resistance to elasticity. Poly(urethane ether)s and poly(ester ether)s are particularly interesting examples of these copolymers. As true elastomers, however, poly(ester ether)s are deficient in terms of the physical properties that are demanded in many applications, particularly when they are melt processed.[3] Specifically, the elastic properties that are deficient in melt-shaped segmented polyester ethers

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are stress and recovery related, such as immediate elastic recovery (often less than 95%), stress decay (often greater than 15%), and compression set (more than 10%). These properties are manifestations of the inefficiency of the physical cross-link in the copolymer, which in turn is a function of how well phase separation is achieved in the copolymer.

Phase mixing can be attributed partly to the irregularity of the copolymer chain. In the case of poly(ester ether) copolymers synthesized by normal step polymerization reactions, the hard segment has a polydispersity ratio approaching 2, and this somewhat broad distribution of chain lengths within the hard segment adversely affects phase separation.[4] Droescher and co-workers support the hypothesis that high regularity within segments, i.e., monodispersity within each segment, leads to enhanced phase separation and crystallization phenomena.[5] Their investigations involved monodisperse aromatic poly(ester ether) copolymers synthesized in a multistep scheme of nucleophilic substitution reactions.[5] Inoue and co-workers[6] also have prepared low molecular weight versions of poly(ester ether) block copolymers having monodisperse segments using porphyrin catalysts. The molecular weights of these polymers are about 5000.

Our goal is to prepare a series of poly(oxyethylene-*co*-pivalolactone) segmented copolymers such that narrow molecular weight distributions (MWD) will be obtained for both segments.[7] The presence of a narrow MWD for the segments increases the likelihood of better phase separation within these copolymers,[4-6] and it may lead to better elastic properties such as immediate elastic recovery, stress decay, and compression set. Depending on the ratio of the segments, these polymers can act as thermoplastic elastomers wherein the poly(oxyethylene) (POE) segment acts as a soft phase and the poly(pivalolactone) (PPVL) segment acts as a hard phase. The POE segment has a lower surface energy than does the PPVL segment, and thus improved phase separation should facilitate the POE segment moving to the surface of the copolymer.[9] This feature is useful in biomedical applications, since POE has much lower platelet adhesion compared to other polymers.[10]

The thrust of our synthetic strategy focuses on the synthesis of a monodisperse poly(oxyethylene-*b*-pivalolactone) telechelomer (a telechelomer is defined as a high molecular weight monomer capable of self-polymerization via a step propagation mechanism) and conversion of it to high molecular weight polymer using step polymerization. The preparation and characterization of telechelomers have been reported earlier.[8]

In this paper we describe the conditions required to convert a telechelomer, I, to a segmented copolymer, II, using step polymerization techniques (Figure 1). Gel permeation chromatograms, intrinsic viscosity data, and ^{1}H and ^{13}C NMR spectra are presented to support the structure of the high molecular weight segmented polymer. Also, differential scanning calorimetry (DSC) is used to discuss the phase separation behavior of the copolymer.

Experimental Section

Step Polymerization. Dry telechelomer, rigorously purified as described previously[8] (0.500 g, 2 × 10^{-4} mol), dry *dl*-alanine (0.016 g, 2 × 10^{-4} mol, Eastman Kodak, purified by crystallization), and a magnetic stirrer were placed in a 10-mL flask (the pressure in the vessel was controlled by using a combination of an argon supply and a vacuum pump). The mixture was dried at 70 °C at 0.1 mmHg of pressure for 2 h and was then brought to atmospheric pressure, and the temperature was raised to 180 °C. The telechelomer melted at this temperature, yet the mixture remained heterogeneous because alanine did not dissolve in the telechelomer. After 2 h, the pressure was reduced to 0.1 mmHg, causing almost all of the alanine to sublime from the mixture, yet leaving behind a catalytic quantity of this amino acid. The contents became clear in about $^1/_2$ h, and at this point, titanium tetrabutoxide (0.004 mL, Alfa, purified by distillation at 135 °C and 1 mmHg) was added quickly, and the mixture was heated to 180 °C at a pressure just below 760 mmHg. In about 1 h, the contents became very viscous, and at this point the temperature was gradually raised to 260 °C. Then a vacuum of 0.1 mmHg was applied, and the contents were stirred for another 30 min. At this point the mixture became too viscous to stir with a magnetic stirrer. The product was a light brown solid, yield = 100% (Anal. Calcd: C, 56.90; H, 8.51. Found: C, 56.86; H, 8.49; N, 0.14).

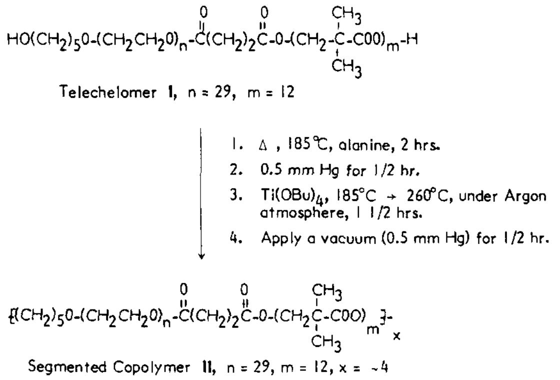


Figure 1. Conversion of telechelomer to segmented copolymer.

Characterization. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were obtained with a Varian XL-Series NMR superconducting spectrometer system. A Waters GPC system containing a Model 6000Å solvent delivery system, coupled with a R-401 *differential refractometer*, was used to obtain GPC chromatograms (solvent, CH$_2$Cl$_2$; flow rate, 1.5 mL/min at 25 °C; columns, 1 × 10^6, 1 × 10^5, 1 × 10^3 Å μStyragel). Intrinsic viscosities were determined by using an Ostwald dilution viscometer at 25 °C with methylene chloride as the solvent. Elemental analysis was done by Atlantic Microlab, Inc.

DSC data were obtained with a Perkin-Elmer 7 Series thermal analysis system equipped with a data station. The instrument was calibrated by a two-point method using cyclohexane and indium. Dry argon was used as the purge gas. A scan rate of 40 °C/min was used. Prior to recording the DSC curve, the sample (9–12 mg) was dropped into liquid N$_2$ from its homogeneous melt at 260 °C, reheated to 260 °C, and cooled to −90 °C at 20 °C/min. Glass transition temperatures, T_g, were provided by the Perkin-Elmer computer program. Crystalline melting temperatures, T_m, were taken as the peak temperatures of the endotherms.

Results and Discussion

The use of activating agents has been a very promising route to carry out polycondensation reactions at lower temperatures. Thus far, a large number of such reagents has been reported for polyesterifications; however, in the course of this work, many of these reagents were proven not suitable for converting the telechelomer to the segmented copolymer due to limitations caused either by the telechelomer or by the activating reagent itself. For instance, chlorinating agents, such as COCl$_2$ and SOCl$_2$, chlorinate not only the –COOH functionality but also the –OH functionality of the telechelomer, thus preventing polyesterification. Some reagents such as chlorosulfonyl isocyanate and methanesulfonyl chloride–(dimethylamino)pyridine require that the hydroxyl functionality be blocked prior to reacting the –COOH functionality, and such a condition could not be met easily in the case of telechelomer, since both functionalities are in the same molecule. Some reagents were not selected because they require solvents that do not dissolve the telechelomer, an example being tosyl chloride/dimethylformamide. Carbodiimides and *N*,*N*′-carbonyldiimidazole have been used very successfully in preparing amides; however, they were not selected because they have some limitations in esterification reactions.[11] Other reagents such as diethyl phosphorocyanidate and unsymmetric anhydrides were not selected because they have been reported to give low yields in polyesterifications.

While we tried a number of activating agents to convert the telechelomer to the segmented copolymer, none of the attempts proved successful. These reagents were (a) -COOH-activating agents such as *N,N'*-bis(2-oxo-3-oxazolidinyl)phosphorodiamidic chloride/triethylamine,[11] 1-methyl-2-bromopyridinium chloride/tri-*n*-butylamine,[12] (b) -OH-activating agents such as triphenyl phosphite[13] and hexachlorocyclotriphosphatriazene,[14] and (c) dehydrating agents such as trifluoroacetic acid/methylene chloride and methylsulfonic acid/phosphoros pentoxide.[15] These agents were investigated with varying reaction times, reaction temperatures, and sometimes with different solvents.

A large number of melt polyesterifications have been reported in the past,[16] and perhaps the one that is used most frequently is two-step melt esterification procedure. First, we attempted to convert the telechelomer to the segmented copolymer without any esterification catalyst, wherein the telechelomer was stirred under vacuum (0.5 mmHg) at 250 °C, for varying periods of time. The maximum reaction time used was 5 h, after which telechelomer degradation occurred. The same set of experiments was carried out in the presence of varying catalytic amounts of antimony trioxide, an important esterification catalyst. These experiments were also unsuccessful. When titanium tetrabutoxide, $Ti(OBu)_4$, was used as a transesterification catalyst, the product formed had a higher intrinsic viscosity than the telechelomer but was still essentially of oligomeric molecular weight. The conditions giving the highest viscosity were (a) $-COOH:Ti(OBu)_4$ ratio of 3000:1, (b) a reaction time of 2 h, and (c) a vacuum of 0.5 mmHg. The esterification with $Ti(OBu)_4$, however, did not yield a product with sufficiently high molecular weight to obtain a solvent cast film.

We assumed that the polyesterification did not proceed to higher conversion because the steric hindrance of the end pivalic acid group obstructed esterification at high viscosities. With a view to overcome this problem, we attempted to convert the end pivalic acid group to a less sterically hindered carboxylic acid group by reacting with *dl*-alanine. We assumed that the amino group in alanine, being more reactive than an alcohol group, would react with the end pivalic acid group of the telechelomer, giving a product with alanine moiety present at one end of the molecule.

In a typical experiment for reacting the telechelomer with *dl*-alanine, equimolar quantities of the two compounds were stirred at 185 °C under argon. Only the telechelomer melted at this temperature; therefore, the reaction mixture was heterogeneous. The temperature could not be increased beyond 185 °C, since alanine sublimed at this temperature. After stirring the mixture for a prescribed period of time, a vacuum was applied to remove any unreacted alanine. The product obtained from this reaction, however, did not form a film when cast from a solution in methylene chloride. When a catalytic amount of $Ti(OBu)_4$ was added to the reaction mixture, just after subliming the unreacted alanine, the viscosity of the mixture increased substantially after a period of 1 h, and the contents could not be stirred with a magnetic stirrer. The product formed a film when cast from a solution in methylene chloride, and the molecular weight of the product, determined by gel permeation chromatography (GPC), was highest under the conditions shown in Figure 1. For instance, when the reaction time was more than 5 h, the product obtained had lower molecular weight as a result of thermal degradation.

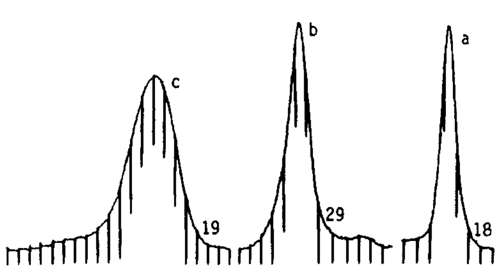
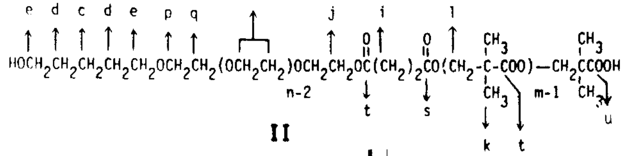


Figure 2. GPC chromatograms (in CH_2Cl_2) at 25 °C; flow rate, 1.5 mL/min; columns, 1×10^5, 1×10^4, 1×10^3 Å μStyragel of (a) PS standard, $\bar{M}_w = 2 \times 10^5$, MWD = 1.04, (b) telechelomer, $\bar{M}_n$ (NMR) = 2670, and (c) segmented copolymer.



$$HOCH_2CH_2CH_2CH_2CH_2OCH_2CH_2(OCH_2CH_2)_{n-2}OCH_2CH_2OC(O)(CH_2)_2CO(O)(CH_2\text{-}C(CH_3)_2\text{-}COO)_{m-1}\text{—}CH_2C(CH_3)_2COOH$$

II

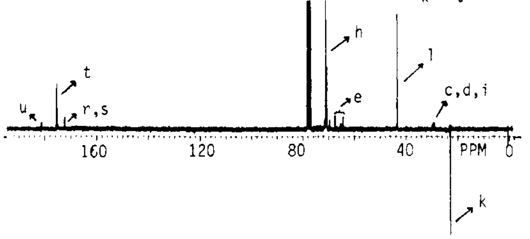


Figure 3. 50-MHz ^{13}C NMR spectrum of the segmented copolymer, II, by using attached proton test sequence (CH_3,CH, negative; CH_2,C, positive) in $CDCl_3$ at 25 °C.

Table I
Solution Properties for the Telechelomer and Segmented Copolymer

compound	η, dL/g	MW
telechelomer	0.06	2700[b]
segmented copolymer	0.32	31000[a]

[a] $\bar{M}_{GPC}$ from universal calibration curve. [b] $\bar{M}_n$ from ^1H NMR.

Figure 2 shows the GPC curves of the telechelomer I, the segmented copolymer, II, and a monodisperse polystyrene (PS) standard of $\bar{M}_w$ = 200 000. The presence of a single peak for the segmented copolymer shows that significant competing reactions were absent during polyesterification. The number average molecular weight of the telechelomer, as determined by ^1H NMR, was 2700, while the molecular weight (M_{GPC}) of the copolymer, as determined by a universal calibration, was 31 000. The GPC curve of the telechelomer shows the presence of some high molecular weight polymer, perhaps due to condensation of the telechelomer upon drying. The [η] of the copolymer was 0.32 dL/g while that of the telechelomer was 0.06 dL/g, nearly a 5-fold increase (Table I).

The ^{13}C NMR spectrum of the segmented copolymer, II (Figure 3), is an attached-proton test (APT) spectrum, which shows secondary and quaternary carbons as upward signals and the tertiary and primary carbons as downward signals. The spectrum was referenced to the solvent ($CDCl_3$) carbon at 77.0 ppm. The major upward signals appearing at 42.9, 69.9, and 176.1 ppm are due to the l, h, and t carbons, and the major downward signal at 21.0 is due to the k carbon.

The smaller signals also could be assigned by using the carbon assignments of the telechelomer,[8] I. For instance,

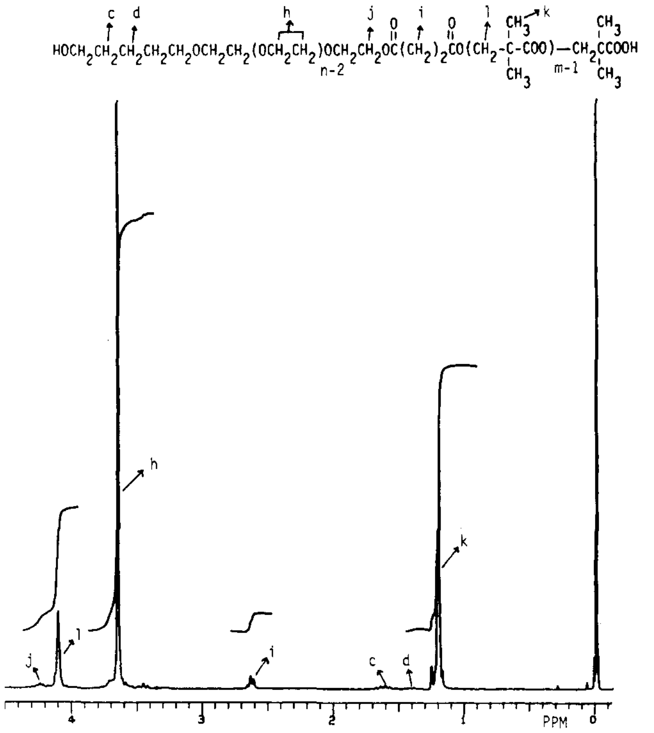


Figure 4. 200-MHz ^{1}H NMR spectrum of the segmented copolymer, II, in $CDCl_3$ at 25 °C.

the upward signals appearing from 29.0–30.0 ppm are due to c, d, and i carbons, and the two upward signals appearing at 64.2 and 67.6 ppm are due to e carbons. The two smaller upward signals surrounding the major h peak are due to p and q carbons which are present in the end ethylene oxides units of the POE segment. The signal at 172.2 is due to carbonyl carbons r and s, and the signal at 181.8 is due to end carboxylic acid carbon u.

The ^{1}H NMR spectrum of the copolymer (Figure 4) also supports the structure II. The larger peaks appearing at 1.2, 3.7 and at 4.1 ppm are due to k, h, and l protons. The multiplets near 1.4 and 1.6 ppm are due to d and c, protons, and the triplets around 2.7 and 4.3 are due to i and j protons. The peaks surrounding the major h signal are due to protons of the end ethylene oxide units in the POE segment.

Elemental analysis agrees well with the calculated values. However, the presence of less than 0.1% nitrogen indicates that a catalytic amount of alanine is left in the copolymer. More alanine can be sublimed from the reaction mixture by increasing the reaction temperature and by stirring more rapidly, but these rigorous conditions degrade the copolymer. The theoretical amount of nitrogen calculated on the basis of a reaction between equimolar quantities of the telechelomer and alanine is 0.5%, and thus it is evident that alanine and the telechelomer did not form a 1:1 adduct. The GPC chromatogram and NMR spectrum of the copolymer clearly show that polyalanine was not formed during the reaction. Alanine is perhaps present as an impurity in the copolymer, because more alanine can be sublimed by increasing the reaction temperature or the vacuum.

The mechanism of this step polymerization is unknown and is still being investigated. $Ti(OBu)_4$ has been used as a transesterification catalyst in the past, but the use of alanine as a catalyst in a polycondensation has not been reported previously. Alanine may be involved in any of the following: (a) acting as a dehydrating agent, (b) acting as a template for the two reacting ends of the telechelomer, (c) increasing the effectiveness of $Ti(OBu)_4$ catalysis. Evidence for alanine acting either as a dehydrating agent or as a template comes from a set of experiments wherein the telechelomer was reacted with alanine in the absence of $Ti(OBu)_4$. These experiments showed that alanine itself caused a slight increase in molecular weight. For instance, the product obtained after the reaction with alanine formed a film when cast from a solution in methylene chloride. Such a film was not formed when the telechelomer was cast from the same solvent. It may be that alanine, being hygroscopic, absorbs water resulting from the polycondensation, or it may be that alanine is acting as a template for the hydroxyl and carboxylic end groups. More experiments are being carried out to differentiate between these two possibilities. The other possible mechanism, i.e., alanine acting as a cocatalyst with $Ti(OBu)_4$ in esterification, is also being examined.

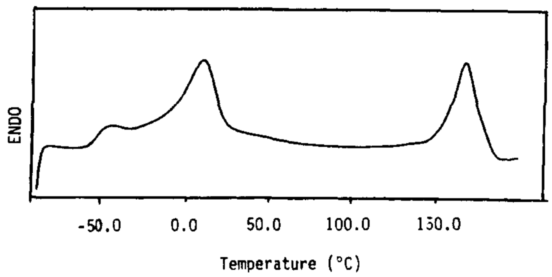


Figure 5. DSC curve of the segmented copolymer. Prior to recording the DSC curve, the sample was dropped into liquid N_2 from 260 °C, reheated to 260 °C, and cooled to −90 °C at 20 °C/min.

The DSC curve of the segmented copolymer (Figure 5) exhibits a glass transition temperature (T_g) for the POE segment appearing at −52 °C and two crystalline melting temperatures (T_m) for the two segments, T_m(POE) and T_m(PPVL), appearing at 6 and 170 °C, respectively. Well-defined melting points for each segment suggest that the copolymer is microphase separated, though the T_g of the POE segment in the copolymer is higher than that of pure POE (−65 to −70 °C).

Is the phase separation between the two segments complete? Previously we reported a method to answer this question for the telechelomer, I, using T_m's as the criteria for phase separation.[20] If there is complete phase separation, the T_m's depend mainly on four factors: (a) the molecular weight of the segment, (b) effect of end groups, (c) copolymerization, and (d) nonequilibrium DSC conditions.[17] If the T_m's of the respective homopolymers are experimentally determined, and they are adjusted for those effects, then the resulting, calculated T_m's are good criteria to determine phase separation. For example, the T_m's of homopoly(oxyethylene) and homopoly(pivalolactone) having molecular weights comparable to those of the segments in the copolymer, are 34 and 191 °C, respectively. The experimentally observed T_m values for these segments in the segmented copolymers, i.e., 6 °C for the POE segment and 170 °C for the PPVL segment, are less than the values obtained by making adjustments to the respective T_m values for the homopolymers. According to this approach, we find that the segments remain mixed to some extent.

Our future work includes the investigation of the function of alanine in step polymerization of the telechelomer. We also plan to further increase the molecular weight of the segmented copolymer.

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Registry No. I (block copolymer), 107558-01-0; Ti(OBu)$_4$, 5593-70-4; alanine, 56-41-7.

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Emulsion Polymerizations. 3. Theory of Emulsion Copolymerization Kinetics[†]

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ABSTRACT: On the basis of an extended Smith–Ewart theory, explicit analytic solutions are derived describing the locus population distribution of emulsion copolymerizing systems. By means of a two-variable transform, the infinite set of partial differential difference equations reduces to a single, highly symmetrical, linear partial differential equation whose solution gives the generating function for the $N_{r,i-r}$ number fraction of loci containing r growing radicals of type A and $i - r$ radicals of type B. Solutions to this equation, in both the stationary and nonstationary state, are given for the pseudohomopolymerization approach and for systems where termination by mutual annihilation is of negligible occurrence. On these grounds, it is concluded that, apart from very special cases, the pseudohomopolymerization approach represents a suitable approximation for systems of practical interest.

Introduction

Since its first appearance 40 years ago, the Smith–Ewart (SE) theory[1,2] has gained wide acceptance as providing a powerful tool to quantitatively describe free-radical compartmentalized polymerization of a wide range of monomers.[3,4] Based on appropriate extensions of this theory, a number of experimentally verified theoretical works now make possible a quantitative understanding and prediction of the dynamic and steady-state behavior of emulsion polymerizing systems. Examples include overall kinetics,[4,5] particle size distribution,[6] molecular weight distribution,[7,8] time evolution of the latex particle formation,[9–11] and so on. In view of the foregoing, apart from intrinsic interest, the extension of the SE theory to emulsion copolymerizing systems not only represents a natural complement but also may nourish advances similar to those made for emulsion homopolymerization. However, this step is not trivial at all. The large number of rate coefficients involved in this process represents a formidable task to the development of a simple mathematical approach to a quantitative description of the overall kinetics of these systems.

A previous paper in this series[12] derived the two-dimensional molecular weight distribution function of emulsion copolymers from a simple probabilistic approach. The distribution of locus population $N_{r,i-r}(t)$, i.e., the number density of reaction loci per unit volume containing r radicals of type A and $i - r$ radicals of type B, has been described through the pseudohomopolymerization approach proposed some years ago by Ballard et al. and Nomura and co-workers.[13] Although this approach seems to represent a quite reasonable approximation for many systems of practical interest, there is still a paucity of knowledge in the space parameter region where this approximation holds true. Accordingly, this paper addresses a solution to the complete SE population balance equations for emulsion copolymers.

For a better understanding of the concepts developed hereafter, it is worthwhile to briefly introduce some fundamental principles of the emulsion copolymerization process. Basically, the time evolution of the locus population distribution is given in terms of simple population balance equations leading to an extended SE theory for copolymers.[13] In the following section the pseudohomopolymerization approach[12,13] will be derived rigorously by introducing an appropriate locus population generating function. Subsequently, it will be shown how the infinite set of differential difference extended SE equations for emulsion copolymers can be reduced to a single, highly symmetrical partial differential equation by applying a suitable two-variable transform. Finally, explicit analytic solutions will be given for the $N_{r,i-r}$ distribution, in both the steady and nonsteady state, for a seeded emulsion copolymerization where the only significant processes that

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[†] For part 2, see ref 12.