melting point depression of 6 °C suggests the possibility for a eutectic mixture having about the same composition as that of the PEO–NaSCN system.

Either system exhibits a nearly vertical salt liquidus curve above the melting point of the solid compound. This reveals that complex formation also takes place in the liquid phase in equilibrium with the solid salt. The apparent coordination number of this complex has been estimated to be close to 4 for NaSCN and close to 5 for KSCN. In the case of the PEO–NaSCN system, it has been possible to rationalize two distinct features related to the liquidus curve of the solid compound in terms of a complex formation in the liquid phase. One of these features is the large χ value of −1.2 derived from the thermodynamic analysis of the P(EO$_3$·NaSCN) liquidus curve by means of Flory–Huggins concepts. The other is the important downward curvature observed in the variation of the latent heat of dissolution of the solid compound as a function of the composition in the subsystem P(EO$_3$·NaSCN)–PEO. Both can be explained by an important exothermic interaction resulting from the solvation of the 3/1 compound by PEO yielding a 4/1 complex in the liquid phase.

As a result of the peritectic reaction that occurs for both systems, bulk recrystallization of the solid compound in mixtures having a salt content greater than that of the peritectic liquid is not a simple liquid–solid phase transition process. Indeed, prior to their solid compound crystallization, all these mixtures, including the stoichiometric mixture, are characterized by the presence of the solid salt dispersed in a liquid phase substoichiometric in salt. This leads to a peculiar situation in which the dissolution rate of the salt, as well as its diffusion rate in the liquid phase, can contribute to a reduction of the rate of crystallization of the solid compound. In this domain of composition, it has been observed that a moderate cooling rate of 40 °C/min is sufficiently rapid for inhibiting the crystallization of the compound with KSCN, while the compound with NaSCN crystallizes readily even at the much greater cooling rate of 320 °C/min. This indicates that diffusion rate of KSCN is considerably smaller than that of NaSCN, a feature that can be explained by the larger size of the potassium ion but also by the greater coordination number of its solvate in the liquid phase. On the other hand, it has been observed that because of the prompt crystallization of the compound with NaSCN, the large NaSCN crystals formed during the first melting of the mixtures are encapsulated by the crystallizing compound and do not participate in the reverse path of the peritectic reaction. Therefore, it appears that contrary to solvent crystallization, bulk crystallization of the stoichiometric mixtures of both systems cannot yield the pure crystalline compounds.

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Model Copolymerization Reactions. Determination of the Relative Rates of Addition of Styrene and Acrylonitrile to the 1-Cyanoethyl Radical

Glenn S. Prementine

Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

David A. Tirrell*

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003. *Received April 13, 1987*

ABSTRACT: 2,2′-Azobis([2-^{13}C]propionitrile) (1) was prepared in 35% overall yield starting from [1-^{13}C]-acetaldehyde (99 atom %). Quantitative ^{13}C NMR analysis of end groups in styrene–acrylonitrile copolymers prepared with 1 as initiator allows determination of the relative rates of addition of these olefins to the 1-cyanoethyl radical. We have found $k_A/k_S = 0.12 \pm 0.03$, a result conistent with the penultimate model treatment of this copolymerization system by Hill, O'Donnell, and O'Sullivan.

Introduction

The development of a thorough understanding of the factors that control the structure of copolymer chains has been frustrated by a lack of analytical methodology capable of discriminating among alternative mechanistic proposals. Following the pioneering efforts of Mayo and Lewis,[1] Alfrey and Goldfinger,[2] and Wall,[3] early workers in the area of radical copolymerization found that their measurements

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of copolymer composition could be rationalized on the basis of the "terminal" kinetic scheme, in which macroradical reactivity is determined solely by the identity of the last-added monomer unit. There followed in the 1950s and 1960s a rapid growth in the copolymerization literature and a growing acceptance of the validity of the terminal model. Almost without exception, this work focused on the prediction, determination, and rationalization of copolymer composition.

Shortly after publication of the terminal kinetic scheme, Merz, Alfrey, and Goldfinger[4] provided an alternative model in which the identity of the penultimate unit on the growing macroradical is taken into account. Although they pointed out that it is not in measurements of composition, but rather "in the length of the [comonomer] sequences that the effect of the monomer in the chain preceding the free-radical chain end would become noticeable...", they concluded that the methods available for sequence analysis were inadequate for quantitative evaluation of kinetic penultimate effects. Despite the passage of four decades, the situation is little different at present, in that most copolymerization studies even now report analyses only of copolymer composition. Sequence distributions are still not routinely accessible, and only very rarely can be determined with accuracy equivalent to that characteristic of composition measurements.

Hill, O'Donnell, and O'Sullivan reported in 1982 a thorough analysis of the copolymerization of styrene (S) and acrylonitrile (A), in which the power of sequence determination was clearly demonstrated.[5] They concluded that the copolymerization is best described by a penultimate kinetic scheme with reactivity ratios $r_{SS} = 0.23$, $r_{AS} = 0.63$, $r_{AA} = 0.04$, and $r_{SA} = 0.09$. These results suggest that the presence of an acrylonitrile unit in the penultimate position depresses the relative affinity of the growing macroradical for acrylonitrile by a factor of about 2.5, regardless of the identity of the terminal unit. While this is not a terribly large substituent effect, neither is it negligible in comparison with the terminal-unit substituent effects generally regarded as dominant in radical copolymerization. In the conventional terminal-model treatment of the radical copolymerization of styrene and methyl methacrylate (M), for example, the relative rates of comonomer addition (k_S/k_M) differ by a factor of about 4 for the two kinetically distinct chain ends.[6] More important, perhaps, is the fact that a penultimate effect of this magnitude influences in a significant way the comonomer sequence distribution.[5]

But are the substituent effects inferred from a kinetic analysis of this kind of any physical significance? Are they consistent with what is known about the behavior of simpler alkyl radicals of analogous structure? In 1985, we reported the results of a series of trapping experiments in which we found that the relative rates of addition of styrene and acrylonitrile to primary alkyl radicals are indeed sensitive to the nature of substituents placed γ to the radical center[7] and that the magnitude of the substituent effect is remarkably similar to that inferred by Hill and co-workers.[5] Specifically, we found that introduction of a cyano group in the γ-position of the radical depressed the relative rate of addition of acrylonitrile by a factor of 3.5.

The present work constitutes part of our effort to extend these measurements to alkyl radicals that reproduce more closely the structures and reactivities of the macroradicals involved in the growth of copolymer chains. We[8] and Bevington and co-workers[9] have reported previously the use of ^{13}C-enriched azo compounds to generate alkyl radicals for kinetic studies. In the present work, we use 2,2′-azobis([2-^{13}C]propionitrile) (1) as a source of the 1-cyanoethyl radical 2. Photolysis of 1 in a mixture of styrene and acrylonitrile leads to free radical copolymerization and to the formation of the two chemically distinct ^{13}C-enriched diads 3 and 4 (eq 1). Four distinct diads are expected if end-group stereochemistry is taken into account. Careful integration of the corresponding ^{13}C NMR signals allows determination of the relative endgroup concentrations and thereby a calculation of the relative rates of addition of styrene and acrylonitrile to the 1-cyanoethyl radical. The results of these experiments are described herein.

Experimental Section

Preparations. 2,2′-Hydrazobis([2-^{13}C]propionitrile) from (1-^{13}C)Acetaldehyde. In a 25-mL glass bottle were placed 10 mL of water, 0.55 g (11.1 mmol) of sodium cyanide, 0.72 g (5.6 mmol) of hydrazine sulfate, and 0.5 g of (1-^{13}*C*)acetaldehyde (99 atom %, MSD Isotopes, Lot no 2804-J). The bottle was tightly stoppered and allowed to stand at room temperature for 3 days. After this time, the reaction mixture was extracted with 3 × 25 mL of ether and dried ($MgSO_4$). Rotary evaporation left 780 mg (100%) of 2,2′-hydrazobis([2-^{13}*C*]propionitrile) as an oil. IR (neat, cm^{-1}): 3285 (N–H stretch), 2990, 2940 (C–H stretch), 2240 ($C{\equiv}N$ stretch). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 120 ($C{\equiv}N$), 48.0, 47.6 (CH); 16.4 (CH_3).

2,2′-Azobis[(2-^{13}C]propionitrile) (1) from 2,2′-Hydrazobis([2-^{13}C]propionitrile). To an ice-cooled three-dram vial were added 300 mg (2.1 mmol) of 2,2′-hydrazobis([2-^{13}*C*]propionitrile) and 0.7 mL of concentrated HCl. This heterogeneous mixture was titrated with Br_2/H_2O with constant vigorous shaking until the bromine color persisted. The mixture was extracted with 75 mL of ether, and the ether layer was washed with 20-mL portions of aqueous sodium bisulfite until the bromine color disappeared. The ether was then removed by rotary evaporation. The resulting wet precipitate was recrystallized from 6:1 methanol/water in a freezer. After filtration, 99 mg (35%) of 2,2′-azobis([2-^{13}*C*]-propionitrile) were obtained; mp 75–77 °C. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.72 (m, 3 H), 4.50 (q, $^1/_2$ H) 5.15 (q, $^1/_2$ H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 116 ($C{\equiv}N$), 62.0 (CH), 16.8 (CH_3). IR (KBr, cm^{-1}): 2990, 2930 (C–H stretch), 2240 ($C{\equiv}N$ stretch). TLC: ($CHCl_3/CH_3OH$, 11:1), one spot, R_f 0.17; (ether/petroleum ether, 1:4), one spot, R_f 0.20. Anal. Calcd for $^{12}C_4{}^{13}C_2H_8N_4$: C, 53.6; H, 5.8; N, 40.6. Found: C, 53.1; H, 7.2; N, 39.8.

Polymerizations. Copolymers. A mixture of 7.5 mg of 1 and 1.0 mL of benzene was placed in a septum-capped glass tube and purged with N_2. A total of 1 mL (14–15 mmol) of purified, N_2-purged monomer was added via syringe. The tube was placed in a thermostated bath in a Rayonet Model RMR 400 photochemical reactor (four 350-nm lamps) for 45 min at 20.0 °C. The polymerization mixtures were then precipitated into methanol and the resulting polymers filtered and reprecipitated into methanol from chloroform solution. The polymers were then dried to constant weight under vacuum. Copolymerization data appear in Table I. Selected copolymers made from unenriched 1 were prepared by identical procedures.

Polystyrene. Styrene (0.5 mL) and 1 (10 mg) were placed in a septum-capped glass tube and irradiated at 350 nm at room temperature for 3 h. The polymer was then isolated and purified as above.

Poly(acrylonitrile). To a glass tube were charged 2 mL of benzene, 0.50 mL of acrylonitrile, and 10 mg of 1. The solution was then irradiated at 350 nm at 20.0 °C for 3 h. The resulting polymer was filtered from the reaction solution and reprecipitated into methanol from dimethyl sulfoxide.

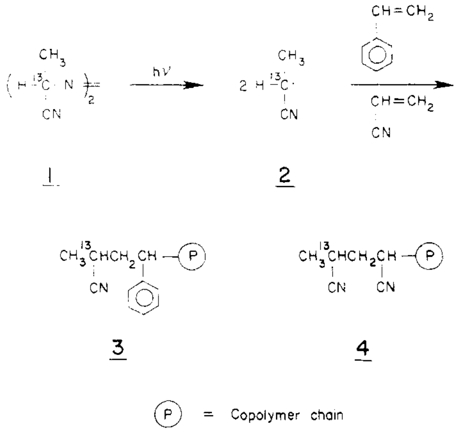
Measurements. ^{13}C NMR spectra of homopolymers were obtained on a Varian XL-200 NMR spectrometer by using a standard single pulse sequence (12-μs pulse width, 1.5-s acquisition time) and broad-band ^{1}H decoupling. Spin–lattice relaxation times (T_1) for end groups 3 and 4 were obtained on a Varian XL-300 NMR spectrometer by using an inversion–recovery technique. The measured T_1 for end group 3 was 0.51 ± 0.02 s. Quantitative ^{13}C NMR spectra of copolymers 1–7 (Table I) were obtained on a Varian XL-300 NMR spectrometer by using a standard single

Table I
Copolymerization Data for ^{13}C-Enriched S-A Copolymers[a]

copolymer	styrene, mmol	acrylonitrile, mmol	acrylonitrile/ styrene ([A]/[S])	yield, mg	convn, %	([4]/[3])[b]
1	1.212	13.381	11.04	109.4	13.1	1.41 ± 0.09
2	1.329	12.906	9.71	62.0	7.5	1.18 ± 0.10
3	1.506	11.986	7.96	45.0	5.7	0.92 ± 0.04
4	1.687	12.273	7.27	80.3	10.1	0.88 ± 0.10
5	1.936	12.604	6.51	27.1	3.1	0.77 ± 0.06
6	2.341	12.349	5.27	55.6	6.2	0.65 ± 0.03
7	2.587	10.698	4.15	13.3	1.6	0.58 ± 0.03

[a] Conditions: 7.5 mg of 1, 1.0 mL of benzene, 20.0 °C, 45 min. [b] Errors are one standard deviation of multiple determinations of relative peak areas.

pulse (14 μs) sequence with gated decoupling to suppress nuclear Overhauser effects (NOE) and a pulse delay of 10 s. End-group signals were assigned on the basis of spectral comparisons with enriched homopolymers and confirmed on the basis of variations in signal intensity with changes in monomer feed composition. Signal integrations were performed by a cut and weigh technique. Peak areas were apportioned between end groups 3 and 4 by drawing vertical lines from local minima to the spectral base line.



Results and Discussion

2,2′-Azobis([2-^{13}C]propionitrile) (^{13}C-APN, 1) was prepared in 35% yield in two steps from commercially available [1-^{13}C]acetaldehyde (99 atom %). Treatment of the enriched aldehyde with aqueous sodium cyanide and hydrazine sulfate afforded a quantitative yield of 2,2′-hydrazobis([2-^{13}C]propionitrile); subsequent bromine oxidation then gave the azo compound. The structure and isotopic enrichment of 1 were confirmed by ^{1}H NMR and ^{13}C NMR spectrometry. The ^{1}H NMR spectrum of 1 contains two methine quartets split by a ^{13}C–^{1}H coupling constant of 152 Hz and centered at δ 4.8, the exact position of the methine proton resonance in the spectrum of unenriched APN. The ^{13}C NMR spectrum of 1 shows an intense signal at 62.0 ppm, the precise chemical shift of the methine carbon atom in the unenriched azo compound.

It was also possible to avoid purchase of the expensive enriched acetaldehyde as the starting material for the preparation of 1. Reduction of [1-^{13}C]acetic acid with thexylchloroborane–methyl sulfide complex,[10] followed by the procedure just described, afforded the enriched azo compound in an overall yield of 8%. The low yield of this procedure, and difficulty in purification of the azo compound derived from it, recommend purchase of the aldehyde as the most efficient route to 1.

2,2′-Azobis(propionitrile) has been reported to be unstable above 30 °C but to decompose upon irradiation at 366 nm to initiate polymerization of styrene with a quantum efficiency of 0.5.[11] We have found APN to serve as an excellent photoinitiator for acrylonitrile as well, though attempts to initiate polymerizations of acrylonitrile or styrene via thermal decomposition were unsuccessful. APN decomposes somewhat more efficiently than does azobis(isobutyronitrile) (AIBN) under our photolysis conditions; we find initiator half-lives of 41 min for AIBN vs 35 min for APN under the conditions used for copolymerization.

We have used APN in its natural-abundance and ^{13}C-enriched forms to prepare homopolymers and copolymers of styrene and acrylonitrile. Copolymerizations were run in benzene solution at 20 °C under steady-state irradiation at 350 nm. Monomer conversions were limited to less than 13%, and all copolymers remained in solution throughout the reaction.

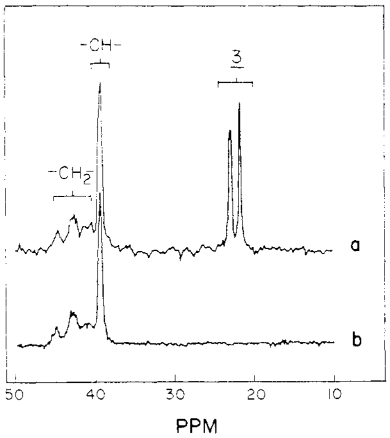


Figure 1. 50-MHz ^{13}C NMR spectra of (a) ^{13}C-enriched and (b) natural-abundance polystyrene in $CDCl_3$. The numbered resonances correspond to end group 3 in eq 1.

Figure 1 shows portions of the ^{13}C NMR spectra of polystyrenes prepared by using enriched and natural-abundance APN. The resonances arising from end group 3 are easily identified at 21.87 and 22.97 ppm in the spectrum of the enriched polymer. The absence of signals at 30–32 ppm argues that there is no significant "head addition" of 1-cyanoethyl to styrene, nor are there important termination or transfer reactions that produce vicinal arrangements of phenyl and cyano substituents at the chain end.

Figure 2 shows ^{13}C NMR spectra of two samples of polyacrylonitrile prepared similarly. The resonances of end group 4 appear at 22.74 and 23.30 ppm in the spectrum of polyacrylonitrile in DMSO-d_6. In this case, information about "head-to-head" arrangements at the chain end would be obscured by the backbone methine carbon signal at 26–28 ppm.

Figure 3 shows the end-group ^{13}C resonances of styrene–acrylonitrile copolymers prepared from two monomer feeds of differing composition. In each case, copolymers were prepared both with natural-abundance APN and with ^{13}C-enriched APN, in order to verify the absence of in-

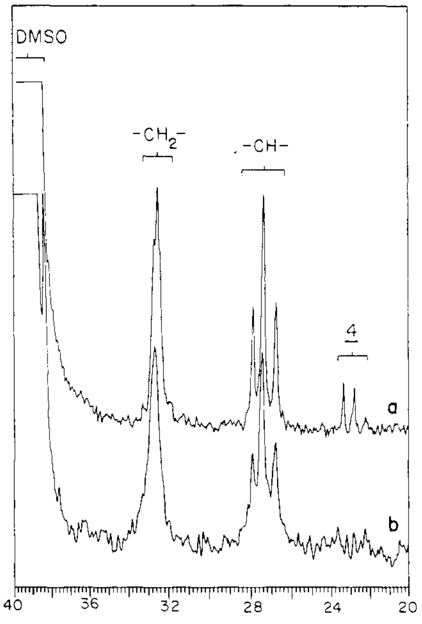


Figure 2. 50-MHz ^{13}C NMR spectra of (a) ^{13}C-enriched and (b) natural-abundance poly(acrylonitrile) in DMSO-d_6. The numbered resonances correspond to end group 4 in eq 1.

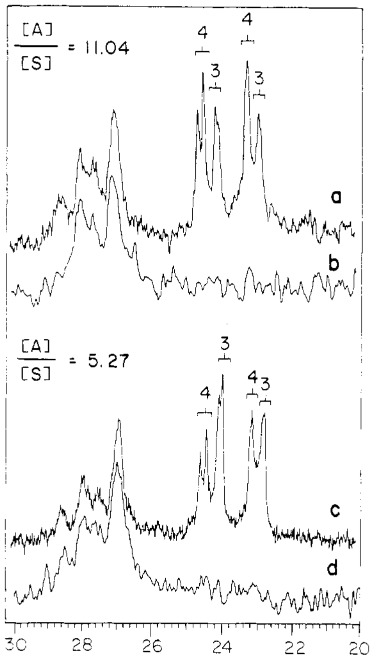


Figure 3. 75-MHz ^{13}C NMR spectra of (a and c) ^{13}C-enriched and (b and d) natural-abundance S–A copolymers in CDCl$_3$ prepared with monomer feed ratios ([A]/[S]) of 11.04 (top) and 5.27 (bottom). The numbered resonances correspond to the end groups in eq 1.

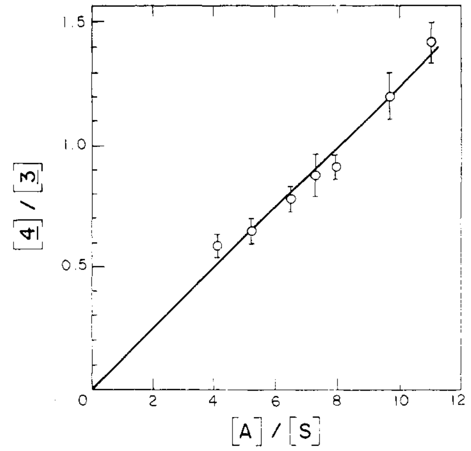


Figure 4. Plot of relative endgroup concentrations ([4]/[3]) vs monomer feed ratio ([A]/[S]) for ^{13}C-enriched S–A copolymers listed in Table I.

terfering signals arising from the copolymer chain backbone. Spectra were recorded with gated decoupling and with a pulse delay of 10 s (20 times the longest endgroup T_1) to ensure the validity of the quantitative treatment of the spectral integration. Assignments of end-group signals were made on the basis of comparisons with homopolymer spectra and by examination of the qualitative changes in signal intensities with changes in monomer feed composition. On this basis, we assign the resonances at 22.75 and 23.93 ppm to end group **3** and those at 23.04, 24.32, and 24.49 ppm to end group **4**. This pattern of end-group signals is reminiscent of our previous work on 1-phenylethyl addition to styrene and acrylonitrile,[8] in which we also observed an analogous **3–4–3–4** line ordering from high field to low. The increased complexity of the end-group signals of the copolymers, i.e. additional splitting in comparison to that observed in the homopolymer spectra, is also consistent with earlier observations.[8]

Careful integration of spectra like those shown in Figure 3 allows the determination of the relative yields of end groups **3** and **4** in each copolymerization. Table 1 summarizes the result of seven such experiments, and Figure 4 shows a plot of the relative end-group concentrations ([**4**]/[**3**]) as a function of the monomer feed composition ([A]/[S]). The plot is linear, as expected, and the slope of the best-fit line gives the relative rates of addition of acrylonitrile and styrene to the 1-cyanoethyl radical (k_A/k_S) as 0.12 ± 0.03.

This rate constant ratio is of some interest when compared to reactivity ratios calculated by the application of conventional kinetic models to the radical copolymerization of styrene and acrylonitrile. The terminal model would demand that k_A/k_S for the 1-cyanoethyl radical should be equivalent to the terminal model reactivity ratio (r_A) for acrylonitrile. On the other hand, the penultimate model would suggest that k_A/k_S for 1-cyanoethyl is not, in the most general case, directly analogous to either of the reactivity ratios (r_{SA} or r_{AA}) assigned to acrylonitrile-terminated macroradicals. Only in the special case where one of the two monomers is kinetically "invisible" in the penultimate position would such an identity be expected.

Our earlier work on the addition of simple primary radicals to styrene and acrylonitrile[7] suggests that this may indeed be a special case of this kind. We found virtually identical reactivity ratios (k_A/k_S) for the 1-butyl and 3-phenyl-1-propyl radicals, a result that suggests that the reactivity pattern is insensitive to the introduction of a phenyl group γ to the radical center. In contrast, k_A/k_S for 3-cyano-1-propyl was depressed by a factor of 3.5, a result consistent with the penultimate kinetic analysis of Hill and co-workers.[5] If this behavior is characteristic of 1-cyano-1-alkyl radicals as well, 1-cyanoethyl should serve as an excellent model of the $\sim$SA$^{\bullet}$ chain end. The behavior of $\sim$AA$^{\bullet}$ would be expected to be perturbed by the γ-cyano group, and correspondence with terminal model reactivity ratios would be precluded by the fact that r_A would have no simple physical meaning.

We note that the value of k_A/k_S determined in the present work is most similar to the penultimate model reactivity ratio r_{SA} reported by Hill and co-workers.[5] Furthermore, this result is consistent with the results of

Table II
Comparison of Observed Reactivity Ratios for 1-Cyanoethyl and 1-Phenylethyl with Reactivity Ratios Calculated from Copolymerization Kinetic Models

radical	k_A/k_S	k_S/k_A	determinatn method	ref
1-cyanoethyl	0.12 ± 0.03		*a*	this work
∼∼A•	0.05		*b*	5
∼∼SA•	0.09		*c*	5
∼∼AA•	0.04		*c*	5
1-phenylethyl		0.20 ± 0.02	*a*	8
∼∼S•		0.33	*b*	5
∼∼SS•		0.23	*c*	5
∼∼AS•		0.63	*c*	5

[a] ^{13}C NMR method described in present work and in ref 8. [b] Calculated from the best-fit terminal model. [c] Calculated from the best-fit penultimate model.

our previous investigation of the 1-phenylethyl radical,[8] in which k_S/k_A was found to be 0.20 ± 0.02—nearly identical with Hill's r_{SS} and significantly different from the terminal model reactivity ratio r_S. Table II compares the observed reactivity patterns of the 1-cyanoethyl and 1-phenylethyl radicals with those calculated for the analogous macroradicals from the kinetic analyses of Hill and co-workers. The comparison lends support to the penultimate model as a physically meaningful description of the radical copolymerization of styrene and acrylonitrile.

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Registry No. 1, 96837-18-2; (S)(A) (copolymer), 9003-54-7; PS, 9003-53-6; PA, 25014-41-9; S, 100-42-5; A, 107-13-1; (1-^{13}C)-H_3CCHO, 2188-31-0; $H_2NNH_2{\cdot}H_2SO_4$, 10034-93-2; 2,2′-hydrazobis([2-^{13}C]propionitrile), 110774-07-7.

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Miscibility and Phase Separation in Poly(vinyl methyl ether)/Poly(bisphenol A hydroxy ether) Blends

C. Uriarte, J. I. Eguiazábal, M. Llanos, J. I. Iribarren, and J. J. Iruin*

Departamento de Química Física y Macromoléculas, Facultad de Ciencias Químicas, Universidad del País Vasco, San Sebastián, Spain. *Received January 6, 1987*

ABSTRACT: Amorphous blends of poly(vinyl methyl ether) ($\bar{M}_w$ = 63 000 and $\bar{M}_n$ = 37 000) and a copolymer of bisphenol A and epichlorohydrin ($\bar{M}_w$ = 50 400 and $\bar{M}_n$ = 18 000) were found to be miscible over the complete range of compositions at temperatures below 420 K. At higher temperatures, blends separate into two phases, giving a LCST-type phase diagram. Heats of demixing and excess heat capacity of a 50:50 blend have also been measured by DSC. The results have been interpreted in terms of the equation-of-state theory and compared with predictions of a recent model proposed by ten Brinke and Karasz for blends which have direction-specific interactions.

Introduction

The blends of a copolymer of bisphenol A and epichlorohydrin (phenoxy) are among the most studied polymer systems. Harris et al.[1] have described numerous miscible and immiscible blends of this polymer with a series of aliphatic and aromatic polyesters. Robeson et al. have reported miscible blends of this polymer with poly(butylene terephthalate) (PBT)[2] and polyethers,[3] such as poly(ethylene oxide) (PEO) and poly(vinyl methyl ether) (PVME). In all cases the stability of such mixtures has been attributed to the intermolecular interactions between the two components of the blend. These interactions would arise from possible hydrogen bonding between the pendant hydroxyl groups of the phenoxy and the carbonyl and ether groups of the second components. Direct evidence of such a hydrogen-bonding interaction has been found in the result of the Fourier transform infrared studies reported by Moskala and Coleman.[4] Robeson et al.[3] noted that the blends of phenoxy and PVME might separate into phases at temperatures of about 200 °C, but they did not present any experimental data for this.

A necessary and sufficient condition for the miscibility of a two-component system is that the second derivative of the Gibbs free energy with respect to the volume fraction of either component should be positive. The equilibrium-phase behavior of polymer–polymer mixtures is, however, primarily governed by the heat of mixing contribution to the free energy. This follows from the fact that, in mixtures of high molar mass polymers, the entropy of mixing is very small positive or even negative.

An exothermic heat of mixing may be the result of two essentially different properties, as ten Brinke and Karasz[5] have pointed out. Miscible blends of homopolymers of sufficiently high molecular weight can only be obtained if some kind of specific interaction exists. These inter-

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* To whom correspondence should be addressed.

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