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References and Notes

(1) Abstracted from a doctoral dissertation submitted by J.-L.C. to the Graduate School of the Polytechnic Institute of New York, June 1982.

(2) (a) Cooper, A. R.; Barrall, E. M. *J. Appl. Polym. Sci.* **1973**, *17*, 1253. (b) Buytenhuys, F. A.; van der Meeder, F. P. B. *J. Chromatogr.* **1978**, *49*, 489. (c) Klein, J.; Westerkamp, A. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 707.

(3) (a) Spatorico, A. L.; Beyer, G. L. *J. Appl. Polym. Sci.* **1975**, *19*, 2933. (b) Cooper, A. R.; Matzinger, D. P. *Ibid.* **1979**, *23*, 419. (c) Dubin, P. L.; Koontz, S.; Wright, K. L. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2047. (d) Rochas, C.; Domard, A.; Rinaudo, M. *Eur. Polym. J.* **1980**, *16*, 135.

(4) Reynolds, J. A.; Tanford, C. *J. Biol. Chem.* **1970**, *245*, 5161.

(5) Weber, K.; Osborn, M. *J. Biol. Chem.* **1969**, *244*, 4406.

(6) (a) Sanger, F. *Science* **1981**, *214*, 1205. (b) Gilbert, W. *Ibid.* **1981**, *214*, 1305.

(7) Ornstein, L. *Ann. N.Y. Acad. Sci.* **1964**, *121*, 321.

(8) Brown, D. W.; Lowry, R. E. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 1039.

(9) Soda, A.; Kagawa, I., as quoted in: Brandrup, J.; Immergut, E. H., Eds. "Polymer Handbook", 2nd ed.; Wiley: New York, 1975; p IV-9.

(10) Rodbard, D.; Chrambach, A. *Anal. Biochem.* **1971**, *40*, 95.

(11) Davis, B. J. *Ann. N.Y. Acad. Sci.* **1964**, *121*, 404.

(12) Peacock, A. C.; Dingman, C. W. *Biochemistry* **1968**, *7*, 668.

(13) (a) Noda, I.; Nagasawa, M.; Ota, M. *J. Am. Chem. Soc.* **1964**, *86*, 5075. (b) Nagasawa, M.; Noda, I.; Takahashi, T.; Shimamoto, H. *J. Phys. Chem.* **1972**, *76*, 2286.

(14) Hermans, J. J. *J. Polym. Sci.* **1955**, *18*, 527.

(15) The relative mobility is here defined using the mobility of the "tracking dye" bromophenol blue as a reference.

Structure of Benzoyl Peroxide Initiated Polystyrene: Determination of the Initiator-Derived Functionality by ^{13}C NMR

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ABSTRACT: The benzoate groups incorporated into polystyrene prepared with benzoyl-*carbonyl*-^{13}C peroxide initiator have been evaluated by NMR spectroscopy. This provides, for the first time, a direct measure of the amounts of initiation by head and tail addition of benzoyloxy radical to styrene as well as a means of determining the extent of transfer to benzoyl peroxide and primary radical termination. For example, polystyrene prepared by bulk polymerization at 60 °C using 0.04 M benzoyl peroxide contains ca. 1.7 benzoate end groups per molecule, 87% of which derive from initiation by tail addition to styrene, 5% by head addition, and 8% by termination through transfer to initiator or primary radical termination. The method also shows the dependence of these processes on reaction conditions.

Introduction

There is an extensive literature on the reaction of benzoyl and other aroyl peroxides with styrene and on the use of these initiators in the preparation of polystyrene. Several studies have been concerned with evaluating details of the polymerization mechanism.[1–11] These investigations concentrated on counting the number of benzoyloxy and phenyl end groups by various techniques and on analyzing the kinetics of the polymerization reaction. Some attempt has been made to correlate these data with what is known about termination. The various effects of "abnormal" termination reactions (transfer to initiator, primary radical termination) have been considered. However, the possibility of nonselectivity in the initiation step has generally been ignored.

Recently, we reported the results of radical trapping experiments that enabled us to outline the pathways by which benzoyloxy and phenyl radicals react with styrene.[12–14] We showed that benzoyloxy radicals react with styrene to afford products from tail addition, head addition, and aromatic substitution (79:6:14) while phenyl radicals give tail addition and aromatic substitution (99:1). In the present paper we show how these pathways are reflected in the structure of polystyrene prepared with benzoyl peroxide as initiator. This has been achieved by using peroxide in which the carbonyl carbon is 90% enriched in ^{13}C and employing NMR to identify and quantify the various types of benzoate groups in the polymer.

Experimental Section

General Procedures. NMR spectra were recorded with a Bruker WM250 or a Varian CFT20 spectrometer. Deuteriochloroform was used as solvent and chemical shifts are reported in parts per million from internal tetramethylsilane. HPLC was performed with a DuPont Model 850 liquid chromatograph that was coupled to an LDC 308 computing integrator. An Altex Ultrasphere ODS column 10 mm × 25 cm was employed, with ethanol/water as eluant. Gel permeation chromatography (GPC) was carried out with a Waters instrument that could be coupled to a Chromatix KMX-6 light scattering photometer and a Chromatix LDS-2 data system. The programs MOLWT and GPCL (Chromatix) were used for data acquisition and reduction. A set of five Waters μ-Styragel columns (10^6-, 10^5-, 10^4-, 10^3-, and 500-Å pore size) was employed and tetrahydrofuran was used as the eluant. Mass spectra were obtained with a Finnigan 3300 spectrometer.

Benzoic-*carboxy*-^{13}C Acid. Benzoic acid enriched in ^{13}C was obtained commercially (Merck Sharpe and Dohme). The degree enrichment was shown by mass spectrometry to be 87 ± 2%.

Benzoyl-*carbonyl*-^{13}C Peroxide. Benzoic-*carboxy*-^{13}C acid (900 mg) was treated with thionyl chloride (1.1 mL), and the mixture was heated at 100 °C for 1 h. The excess thionyl chloride was then evaporated and the residue distilled to give benzoyl-*carbonyl*-^{13}C chloride: 940 mg, 90%; bp 170 °C (100 mmHg).

This product (900 mg) was slowly added to a solution of sodium peroxide (400 mg) in water (7 mL) and benzene (1 mL) at 5 °C and the mixture stirred for 90 min. The mixture was then extracted with benzene, and the extract was washed with water, dried ($MgSO_4$), and evaporated. The crude peroxide was dissolved in chloroform and precipitated with methanol at 0 °C to give benzoyl-*carbonyl*-^{13}C peroxide: 650 mg, 84%; ^{13}C NMR δ 163.1 (C=O).

Polymerizations. Freshly distilled styrene was degassed and then distilled into an ampule containing the appropriate amount of benzoyl peroxide on a vacuum line operating at 10^{-6} mmHg. The ampule was degassed by the freeze–thaw technique, sealed, and immersed in a constant-temperature bath at 60.0 ± 0.1 °C. Polystyrene samples A, B, C, D, and E were prepared by using 0.01, 0.04, 0.1, 0.1, and 0.1 M benzoyl peroxide and reaction times

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Table I
^{13}C Chemical Shifts of Benzoate Ester Carbonyl Carbons (PhCO_2R)[a]

primary benzoates		secondary benzoates		tertiary benzoates		aromatic benzoates	
R	chem shift	R	chem shift	R	chem shift	R	chem shift
ethyl	166.5	isopropyl	165.9	*tert*-butyl	165.6	phenyl	165.0
2-phenylethyl	166.3	1-phenylethyl	165.6	1-methyl-1-phenylethyl	165.1	2-isopropylphenyl	165.1
1	166.3	2	165.8			4-isopropylphenyl	165.1
		1,3,5-triphenylpentane-1,5-diyl[b]	165.4, 165.5			*p*-(benzoyloxy)styrene/styrene copolymer	164.9

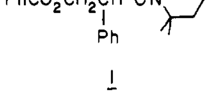
[a] Chemical shifts in ppm relative to internal Me_4Si. [b] Mixture of stereoisomers.

of 295, 150, 92, 470, and 960 min, respectively.[1,2] The polymer was precipitated with methanol, dissolved in benzene, and reprecipitated with methanol three times. The yields of polymers A–C were ca. 8% and those of polymers D and E were ca. 30% and 80%, respectively, based on styrene.

Molecular Weight Determinations. The molecular weights of polystyrene samples were determined both by GPC and by coupled GPC/low-angle light scattering measurements. The numbers obtained by the two methods were in good agreement (±5%). The numbers shown in Table II are the average of two or more determinations. Both methods were calibrated by chromatography of narrow distribution polystyrene standards (Waters).

Polystyrene NMR. The 62.9-MHz NMR spectra were obtained by using a nuclear Overhauser enhancement suppression pulse sequence in which the broad-band decoupler was on during relaxation delay and off during acquisition (inverse gated decoupling). The resulting spectra are thus fully decoupled and yet without nuclear Overhauser enhancement. In addition, a series of experiments were carried out to ascertain the optimum relaxation delay (>10 s) such that the relative peak intensities are not influenced by the relatively long T_1 of the benzoate carbonyl. As a consequence, the observed peak intensities are directly proportional to carbon concentrations. These were evaluated directly by integration of the NMR spectra in the case of separate peaks and by triangulation in the case of fused peaks. The spectra were recorded over spectral widths of 12 000 Hz with 32K data points and typically required the accumulation of 15 000–20 000 transients.

Radical Trapping Experiment. The following procedure was used. Benzoyl-*carbonyl*-^{13}C peroxide (49.6 mg) was added to a solution of the nitroxide 2,2,6,6-tetramethylpiperidinyl-1-oxy (65.4 mg) in freshly distilled styrene (10 mL). The resultant solution was degassed by the freeze–thaw technique, sealed under vacuum (0.01 mmHg), and placed in a constant-temperature bath at 60.0 ± 0.1 °C until the benzoyl peroxide was completely consumed (ca 2 h). The mixture was concentrated to ca. 0.5 mL at low temperature (40 °C (10 mmHg)) and analyzed by HPLC. The products were identified by comparison of their ^{1}H and ^{13}C NMR spectra and HPLC retention with those of the unlabeled analogues. These latter compounds have been fully characterized by spectral and analytical data of samples isolated by preparative HPLC and, where possible, by comparison with authentic samples.[12,13] For the NMR measurements all the residual styrene and excess nitroxide were removed under vacuum (40 °C (0.1 mmHg)). The 62.9-MHz ^{13}C NMR spectrum of the mixture shows peaks at δ 167.2, 166.3, 165.7, 165.1, and 164.9, corresponding to the carbonyl carbons of benzoic acid, compounds 1 and 2, *o*-(benzoyloxy)styrene, and *m*- and *p*-(benzoyloxy)styrenes (not resolved). Integration of the NMR spectrum showed the relative yields of these compounds to be 52, 39, 3, 3, 1, and 3%, respectively, in excellent agreement with the HPLC determination.[12-14]



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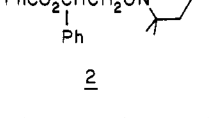

2

Benzoate Esters. The benzoate esters shown in Table I either were commercial samples or were obtained by esterification of the appropriate alcohol or phenol using standard procedures.

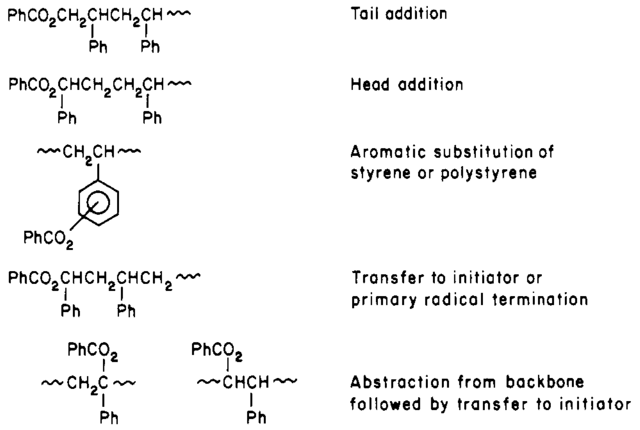

Figure 1. Types and sources of benzoate groups in polystyrene.

Results and Discussion

In order to get a direct measure of the number and type of benzoate groups in polystyrene, we have prepared samples of polymer using benzoyl-*carbonyl*-^{13}C peroxide. Most polymerizations were carried to only low conversion so that the yield of products from the interaction of benzoyloxy radicals with polymer should be negligible (see below).

Our previous work[12,13] indicated that polystyrene prepared with benzoyl peroxide initiator can contain three different types of benzoate groups. These arise from (a) initiation by addition of benzoyloxy radical to the less substituted end of the styrene double bond (tail addition), (b) addition to the more substituted end of the double bond (head addition), and (c) aromatic substitution of styrene or polystyrene. In addition, we expect that there will be benzoate end groups resulting from termination by transfer to initiator and by primary radical termination.[1,2] The latter end groups differ from those formed by head addition in that the first two phenyl groups along the polymer chain from the benzoate group are in a 1,3 vs. a 1,4 relationship (see Figure 1). We have shown previously[13] that both of the radicals formed by benzoyloxy radical adding to the styrene double bond react with a second molecule of styrene by tail addition.

The ^{13}C NMR spectra of the polymers A–D show six resonances in the region δ 165–167 typical of benzoate esters. The two largest peaks, at δ 166.2 and 166.3, are assigned to stereoisomeric (see below) primary benzoate carbonyls arising from tail addition of benzoyloxy radical while those at δ 165.3, 165.4, 165.5, and 165.6 are attributed to secondary benzoate carbonyls, which can be formed by head addition, transfer to initiator, or primary radical termination. These assignments are consistent with the fact that primary, secondary, tertiary, and aromatic benzoate carbonyls have characteristic chemical shifts[15] (see Table I).

Two peaks are observed for the primary benzoate carbonyls that arise by tail addition. This is due to the fact that the benzylic radical formed by addition of benzoyloxy

Table II
Relative Amounts of Benzoate Groups Formed during Styrene Polymerization at 60 °C Using Benzoyl Peroxide Initiator[a]

sample	[I],[b] M	% conv	tail addition	head addition	other processes[c]	mol wt[d]	end groups per molecule[e]
A	0.01	8	91	5	4	170 000 (210 000)	1.4
B	0.04	8	87	5	8	81 000 (84 000)	1.7
C	0.1	8	82	4	14	45 000 (47 000)	1.5
D	0.1	30	78	4	18	44 000 (48 000)	1.6
E	0.1	80	57	3	38[f]	46 000 (—)	2.3

[a] Evaluated by determining the relative intensity of the resonances due to the corresponding benzoate carbonyl carbons in the ^{13}C NMR spectra of the polymers (see text). [b] Initial concentration of benzoyl peroxide. [c] Includes transfer to initiator and primary radical termination (see text). [d] Number-average molecular weight ($M_w/M_n = 1.6$); data obtained by coupled GPC/low-angle light scattering measurements are given in parentheses. [e] Determined by integrating the total intensity of the peaks due to the benzoate carbonyl carbons relative to that of the C-1 aromatic carbon of polystyrene and taking into account the degree of enrichment of the benzoyl peroxide used and the molecular weight of the polymer. [f] Includes aromatic substitution (ca. 2% of total).

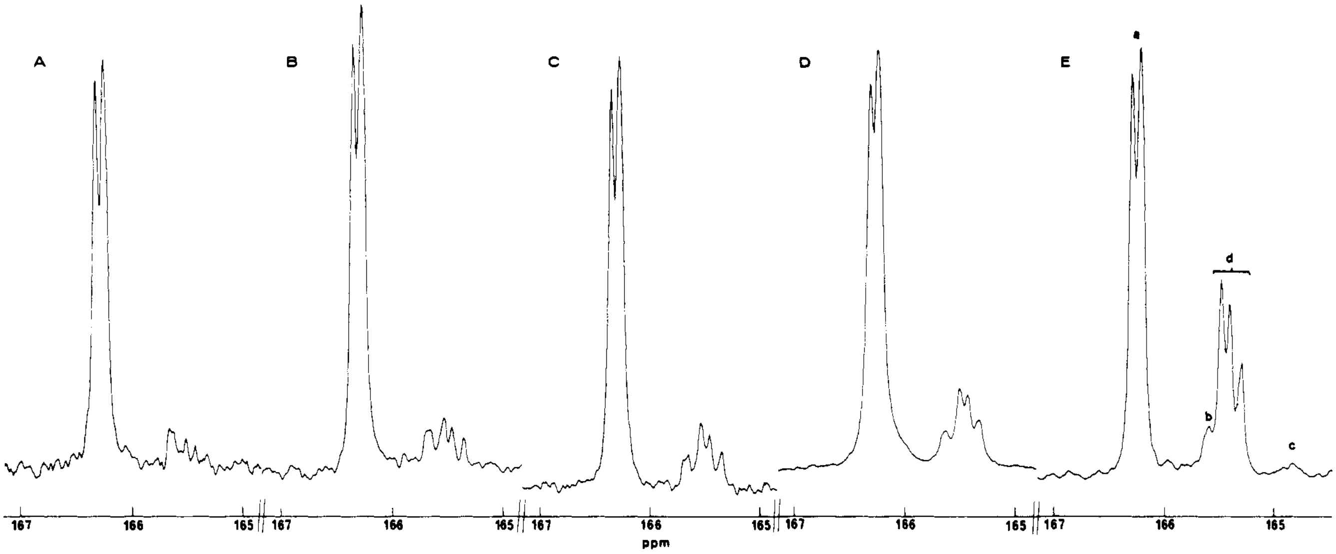

Figure 2. Carbonyl region of ^{13}C NMR spectra of polystyrene samples A–E. Assignments are as follows: (a) carbonyl of benzoate group from tail addition; (b) head addition; (c) aromatic substitution; (d) transfer to benzoyl peroxide or primary radical termination (refer to Figure 1).

radical to styrene adds to another molecule of styrene to produce a chiral center and, similarly, each subsequent propagation step also gives a new chiral center. The observation that the two peaks are of approximately equal intensity indicates that there is a similar proportion of "meso" and "*dl*" chain ends. That is, the stereochemistry of the first addition reaction does not influence significantly the course of the second, which is in accord with the observation[16] that radical-inititated polystyrene is essentially atactic. We can similarly rationalize the broadness of the peak attributed to the carbonyl of the benzoate end group formed by head addition to styrene and the multiple peaks due to the benzoates from transfer to initiator (see below).

The proportion of benzoate end groups that derive from head vs. tail addition will be independent of the initiator concentration, whereas the number arising by transfer to initiator, primary radical termination, or aromatic substitution will be a function of the initiator concentration employed in the preparation of the polymer. On this basis, the single broad resonance at δ 165.6 is assigned to the benzoate carbonyls from head addition since, as is apparent from Figure 2 and Table II, it remains of constant intensity relative to the resonances at δ 166.2 and 166.3 (assigned to the benzoate carbonyls from tail addition) in each of the polystyrene samples A–E. If we accept this assignment, the amount of head vs. tail addition is in accord, within the limits of experimental error, with that determined in our investigation of the reaction of benzoyloxy radicals with styrene using the radical trapping technique.[12,13]

In contrast, the intensities of the resonances at δ 165.4, 165.4, and 165.5 show dependence both on the amount of initiator used in preparation of the polymer and on the degree of conversion. These resonances are therefore assigned to benzoate carbonyls arising from transfer to initiator and/or primary radical termination.

The reaction of benzoyloxy radicals with the aromatic ring of styrene is reversible.[12,13] Whereas in the presence of (for example) nitroxide radical scavengers the cyclohexadienyl radicals formed by aromatic substitution are efficiently oxidized to (benzoyloxy)styrenes,[13] in the absence of such species the oxidation of the cyclohexadienyl radicals may not be competitive with their reversion to starting materials. This, coupled with the fact that the polymerizations were only carried to low conversion, explains why no resonances attributable to the aromatic benzoate carbonyls of copolymerized (benzoyloxy)styrene can be seen in the NMR spectra of samples A–D.

We can also exclude the possibility that, in these circumstances (low conversion), any significant fraction of benzoate groups observed by NMR is formed through the interaction of benzoyloxy radicals with polystyrene (by aromatic substitution or abstraction followed by transfer to initiator).[17] The proportion of such products should show a direct dependence on the degree of conversion (i.e., the relative concentrations of styrene and polystyrene) whereas we find for the polystyrene samples C and D (8 and 30% conversion, respectively) that the relative yield of the various benzoate ester groups is essentially the same (see Figure 2).

For sample E (80% conversion) we note a marked increase in the intensity of the resonances ascribed to the benzoate groups that arise by transfer to initiator and primary radical termination and the appearance of resonances in the region δ 164.8–165.0, which are probably due to aromatic benzoate carbonyls. The available data do not enable us to distinguish whether these arise from copolymerized (benzoyloxy)styrenes or from attack of benzoyloxy radicals on polystyrene. An increase in the total number of benzoate groups per molecule for this sample (see Table II) suggests that, under these conditions of high conversion, a significant amount of grafting also occurs (presumably initiated by benzoyloxy (or phenyl) radicals abstacting a hydrogen from polymer) to give molecules of polystyrene with three or more initiator residues.

The relative number of benzoate groups incorporated into each of the polystyrene samples A–D (determined by integration of all resonances in the carbonyl region vs. that due to the C-1 aromatic carbon of polystyrene) varies in the expected way with molecular weight. The absolute number of end groups per molecule cannot be evaluated with great accuracy. However, the number obtained (1.6 ± 0.2; see Table II), after the degree of enrichment of the peroxide used is taken into account, is in reasonable agreement with the value of 1.7–1.9 expected if termination occurs primarily by combination or transfer to initiator.[18] In this context, it should be noted that, since a proportion of benzoyloxy radicals will decarboxylate to give phenyl radicals before reacting with monomer, a portion of polystyrene chains will terminate in phenyl groups. These end groups cannot be determined by the present procedure, although, on the basis of other data, they should amount to less than 4% of the number of benzoate end groups.[3,13]

The amount of transfer to benzoyl peroxide indicated by our experiments (see Table II) is slightly less than predicted on the basis of the literature value for the transfer constant C_I. Calculations carried out by Pryor et al.[2,9] in this regard indicate that, for polymerizations carried to 8% conversion with 0.01, 0.04, and 0.1 M benzoyl peroxide, approximately 6, 10, and 15% of polymer chains, respectively, will have secondary benzoate end groups derived from transfer to initiator. It can be noted that, since a significant proportion of polymer chains will be initiated by head addition to styrene, there will be a proportion of polymer chains with secondary benzoate end groups even under conditions where there is minimal transfer to initiator. The presence of this functionality may be relevant to the thermal stability of polystyrene.[13,19,20]

In conclusion, an NMR technique has been developed that enables the initiator-derived functionality in vinyl polymers to be readily determined. We have demonstrated our method by evaluating the types of benzoate groups that are present in polystyrene which has been prepared with benzoyl peroxide as initiator. We are currently extending our work to cover other initiators and monomers and will report on these in the near future. It is hoped that this work will lead to a better understanding of the manner in which the structure and properties of polymers depend on the conditions used in their preparation.[19-24]

Note Added in Proof. In a recent communication that appeared while the present work was in press, Bevington et al. reported on the ^{13}C NMR spectra of polystyrene and poly(methyl methacrylate) prepared with azobis(isobutyronitrile-β,β-^{13}C) (Bevington, J. C.; Ebdon, J. R.; Huckerby, T. N.; Hutton, N. W. E. *Polymer* **1982**, *23*, 163–164).

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References and Notes

(1) Mayo, F. R.; Gregg, R. A.; Matheson, M. S. *J. Am. Chem. Soc.* **1951**, *73*, 1691–1699.
(2) Pryor, W. A.; Coco, J. H. *Macromolecules* **1970**, *3*, 500–508.
(3) Bevington, J. C.; Jemmett, J. A. L. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1866–1871.
(4) Allen, J. K.; Bevington, J. C. *Trans. Faraday Soc.* **1960**, *56*, 1762–1769.
(5) Boyer, R. F.; Simha, R. In "Styrene"; Boundy, R. H., Boyer, R. F., Eds.; Reinhold: New York, 1952; p 411.
(6) Kaemmerer, H.; Rocaboy, F.; Steinfort, K. G.; Kern, W. *Makromol. Chem.* **1962**, *53*, 80–90.
(7) Anisimov, Y. N.; Ivanchev, S. S.; Yurzhenko, A. I. *Polym. Sci. USSR (Engl. Transl.)* **1967**, *9*, 773–780.
(8) Baysal, B.; Tobolsky, A. V. *J. Polym. Sci.* **1952**, *8*, 529–541.
(9) Pryor, W. A.; Fiske, T. R. *Macromolecules* **1969**, *2*, 62–70.
(10) Berger, K. C.; Deb, P. C.; Meyerhoff, G. *Macromolecules* **1977**, *10*, 1075–1080.
(11) Deb, P. C.; Gaba, I. D. *Makromol. Chem.* **1978**, *179*, 1549–1557.
(12) Moad, G.; Rizzardo, E.; Solomon, D. H. *J. Macromol. Sci., Chem.* **1982**, *17*, 51–59.
(13) Moad, G.; Rizzardo, E.; Solomon, D. H. *Macromolecules* **1982**, *15*, 909.
(14) Moad, G.; Rizzardo, E.; Solomon, D. H. *Tetrahedron Lett.* **1981**, *22*, 1165–1168.
(15) Pelletier, S. W.; Djarmati, A.; Pape, C. *Tetrahedron* **1976**, *32*, 995–996.
(16) Randall, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1975**, *13*, 889–899.
(17) Haas, H. C. *J. Polym. Sci.* **1961**, *54*, 287–299.
(18) Gleixner, G.; Olaj, O. F.; Breitenbach, J. W. *Makromol. Chem.* **1979**, *180*, 2581–2590.
(19) Jellineck, H. H. G. In "Styrene"; Boundy, R. H., Boyer, R. F., Eds.; Reinhold: New York, 1952; p 649.
(20) Singh, M.; Nandi, U. S. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 121–124.
(21) Wall, L. A.; Straus, S.; Florin, R. E.; Fetters, L. J. *J. Res. Natl. Bur. Stand., Sect. A* **1973**, *77* 157–170.
(22) Cascaval, C. N.; Straus, S.; Brown, D. W.; Florin, R. E. *J. Polym. Sci., Part C* **1976**, *57*, 81–88.
(23) Cameron, G. G.; Meyer, J. M.; McWalter, I. T. *Macromolecules* **1978**, *11*, 696–700.
(24) Rudin, A., Samanta, M. C.; Reilly, P. M. *J. Appl. Polym. Sci.* **1979**, *24*, 171–185.