Macromolecules 1985, *18*, 1659-1663

Cationic Polymerization of Para-Substituted α-Methylstyrenes. 6. Solvent Polarity Effects on Polymer Tacticity

R. W. Lenz,* D. J. Fisher, and J. M. Jonte[†]

Chemical Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003. *Received February 13, 1985*

ABSTRACT: The effect of solvent polarity on polymer tacticity in the cationic polymerization of para-substituted α-methylstyrenes was investigated. Triad tacticities were interpreted on the basis of the existence of either ion pair or free ion active end groups. For *p*-chloro-α-methylstyrene, solvents of higher polarity favoring solvation of ion pairs yielded polymers of high syndiotacticity, and solvents of increasingly lower polarity gave polymers of increased heterotactic and isotactic contents. In the case of the *p*-fluoro-substituted polymers, no change in polymer tacticity was observed over the same range of solvent polarities. An abrupt change in tacticity over a narrow solvent mixture range for the *p*-chloro monomer was caused by precipitation of the polymer from the reaction solution. Tacticity changes for the *p*-chloro monomer were continuous under homogeneous conditions.

Introduction

Recent studies in this laboratory have shown that both the presence of different types of para-substituents and variations in the initiator/coinitiator system can have large influences on the tacticity of para-substituted α-methylstyrene polymers prepared by cationic polymerization reactions.[1] In the reactions reported in those studies, generally only one solvent was studied extensively, methylene chloride. Earlier work[2,3] on the polymerization of *p*-methyl- and *p*-chloro-α-methylstyrene showed that substantially lower syndiotactic contents were obtained with toluene or heptane as solvents, but no systematic study was made of the use of solvent mixtures to vary the dielectric constant of the reaction medium.

To obtain more information on solvent effects in these systems, two series of polymerization reactions with *p*-chloro- and *p*-fluoro-α-methylstyrene monomers were performed in the present study using various mixtures of methylene chloride (dielectric constant $\epsilon = 14.8$) and hexane ($\epsilon = 2.0$) or methylene chloride and toluene ($\epsilon = 2.6$) as solvents for the reactions. The values of ϵ for the pure solvents at the polymerization temperature of −78 °C were calculated from the following equations:[4]

$$\text{methylene chloride} \qquad \epsilon = 3320/T - 2.24 \tag{1}$$

$$\text{hexane} \qquad \epsilon = 2.35 - T/625 \tag{2}$$

$$\text{toluene} \qquad \epsilon = 2.438 \text{ invlog } (-0.455 \times 10^{-2}T) \tag{3}$$

The ϵ values for the various mixtures were calculated by linear interpolation. The tacticities of the polymer samples were determined by proton NMR spectroscopy based on the α-methyl group resonances.[5,6]

A reasonable mechanism by which tacticity could be related to the type of ion pair of the active end group in propagation was proposed by Kunitake and Aso[7] based on preferred conformations of the terminal units caused by steric crowding and either "front-side" or "back-side" attack by the monomer on the ion pair. According to their proposal, free ions or solvated ion pairs should form syndiotactic diads preferentially and contact ion pairs should form isotactic diads preferentially.[8] Thus, a direct relationship should exist between triad tacticity and the nature of the ion pair that formed the polymer. Therefore, the results of our earlier studies indicate that, for the cationic polymerization reactions carried out in methylene chloride on several different types of para-substituted α-methylstyrenes, the formation of highly syndiotactic polymers is indicative of propagation by either free carbocations or solvated ion pairs, and decreasing solvent polarity should directly affect tacticity.

Results and Discussion

***p*-Chloro-α-methylstyrene.** Experimental results obtained from a series of polymerization reactions with varying solvent compositions for *p*-chloro-α-methylstyrene with tin tetrachloride as initiator are collected in Table I. These reactions were conducted in solvent mixtures over the entire range of compositions from pure methylene chloride to pure hexane, for which ϵ values ranged from 14.8 to 2.0. The polymers formed in the solvent mixtures of higher polarity, $\epsilon > 12.2$, had syndiotactic triad contents of approximately 90% and isotactic triad contents of only 1%–2%.[9] In solvent mixtures of lower polarity, $\epsilon < 12.2$, however, the syndiotactic triad contents dropped abruptly, the heterotactic triads increased, and the isotactic triads reached a maximum of approximately 10%.

This change in tacticity levels presumably represented the occurrence of an abrupt change in propagation mechanism. What is most surprising in these data is the sharpness of the change in tacticity values. Within a change of dielectric constant of only 0.3 for reactions 5 and 6, the syndiotactic level decreased 12% and the isotactic content increased by 6% after showing almost no change over the range of ϵ values from 14.8 to 12.2. Further studies showed that upon addition of increasing amounts of hexane to methylene chloride for the reaction solvent, the polymerization media became heterogeneous in the narrow range between $\epsilon = 12.1$ and 12.3. This heterogeneity appears to be the cause of the large decrease in the yields of the polymers in the range $\epsilon = 12.2$–12.1 as shown in Table I, and precipitation of a polymer by a nonsolvent is known to occur sharply over a narrow range of added nonsolvent.[10]

In light of the precipitation of the polymer at higher hexane content in the reaction solvent, the abrupt changes in polymer tacticity can be explained. That is, it is apparent that, at higher methylene chloride content, the polymerization reaction occurs in a homogeneous phase in which the carbocation is in an environment of the polar solvent that is conducive to syndiotactic placement. At hexane content greater than 20% by weight, however, the reaction medium becomes heterogeneous because of precipitation of the polymer, and propagation occurs in a low-polarity environment, which is more conducive to isotactic placement. The former environment may involve a free or solvated carbocation while the latter a contact ion pair, but very little is known about such species because of their extremely short lifetimes.[11]

[†] Present address: Institut für Angewandte Chemie, Universität Hamburg, D-2000 Hamburg, West Germany.

0024-9297/85/2218-1659$01.50/0

Table I
Effect of Solvent Composition on the Cationic Polymerization of *p*-Chloro-α-methylstyrene in Methylene Chloride–Hexane Mixtures Initiated with $SnCl_4$

	solvent comp, wt %				triad tacticity			
reactn no.	CH_2Cl_2	hexane	ϵ^a	polym yield, %	P_S	P_H	P_I	σ^b
1	100	0	14.8	97	0.92	0.07	0.01	0.04
2	98	3	14.5	98	0.96	0.03	0.01	0.02
3	82	18	12.5	33	0.93	0.05	0.02	0.04
4	80	20	12.2	85	0.92	0.07	0.01	0.04
5	80	20	12.2	51	0.89	0.09	0.02	0.06
6	79	21	12.1	10	0.77	0.15	0.08	0.16
7	77	23	11.9	2	0.72	0.22	0.06	0.17
8	77	23	11.9	8	0.74	0.17	0.09	0.18
9	67	33	10.6	5	0.68	0.23	0.09	0.20
10	54	46	8.9	7	0.63	0.28	0.09	0.23
11	50	50	8.4	9	0.64	0.27	0.09	0.22
12	46	54	7.9	2	0.61	0.31	0.08	0.24
13	6	94	2.8	3	0.55	0.35	0.10	0.28
14	0	100	2.0	0				

[a] Calculated dielectric constant of solvent mixture. [b] Calculated from triads: $\sigma = P_I + {}^1/_2P_H$.

Table II
Effect of Solvent Composition on the Cationic Polymerization of *p*-Chloro-α-methylstyrene in Methylene Chloride–Toluene Mixtures Initiated with $SnCl_4$

	solvent comp, wt %				triad tacticity			
reactn no.	CH_2Cl_2	toluene	ϵ^a	polym yield, %	P_S	P_H	P_I	σ^b
15	100	0	14.8	88	0.91	0.09	0	0.04
16	98	2	14.6	57	0.89	0.11	0	0.06
17	83	17	12.7	37	0.87	0.13	0	0.06
18	60	40	9.9	6	0.85	0.15	0	0.08
19	13	87	4.2	*c*	0.79	0.18	0.03	0.12
20	5	95	3.2	*c*	0.73	0.23	0.04	0.16

[a] Calculated dielectric constant of solvent mixture. [b] Calculated from triads: $\sigma = P_I + {}^1/_2P_H$. [c] Obtained after 1-h reaction time.

To circumvent the problem of polymer precipitation with decreasing polarity of the reaction medium, a solvent system was chosen in which the polymer is soluble over the entire range of dielectric constants used. Poly(*p*-chloro-α-methylstyrene) is soluble in 100% toluene at −78 °C, and the dielectric constant of mixtures of methylene chloride and toluene can be varied over a range of ϵ values of 14.8–2.6, similar to those values of ϵ obtained with the mixtures of methylene chloride and hexane.

Experimental results for a series of polymerization reactions with toluene as the added solvent for *p*-chloro-α-methylstyrene, again with tin tetrachloride as initiator, are presented in Table II. The solvent mixtures used comprised the range of compositions from pure methylene chloride to 95% toluene by weight, for which the ϵ values ranged from 14.8 to 3.2. At $\epsilon < 4.2$, no polymer formed after the reaction time of 5 min. The polymers of reactions 19 and 20 were obtained after a reaction time of 1 h, but investigations in this[12] and other[13] laboratories have shown that tacticity is not a function of conversion for α-methylstyrene type monomers. Therefore, the tacticities of the polymers obtained in reactions 19 and 20 may be compared for solvent effects with those of reactions 15–18. The polymers formed in high-polarity mixtures showed a high syndiotactic content as before, but for this system, as the solvent polarity decreased the syndiotactic content decreased continuously while the heterotactic content increased slightly and the isotactic content increased to only 4% at $\epsilon = 3.2$. This smooth change of tacticities is in direct contrast to the abrupt tacticity changes for the polymers obtained in methylene chloride–hexane mixtures.

This contrast is shown in Figures 1 and 2. In Figure 1, the triad tacticity for the polymers formed in mixtures of methylene chloride and hexane is plotted against the dielectric constant, ϵ, over the range of solvent mixtures. As seen in the figure, the syndiotacticity showed little change at first but then dropped sharply at $\epsilon = 12.2$ concurrent with polymer precipitation. Figure 2 contains the same data for the polymers obtained in mixtures of methylene chloride and toluene. In this figure, all tacticity changes are smooth and fairly small over the range of ϵ values studied.

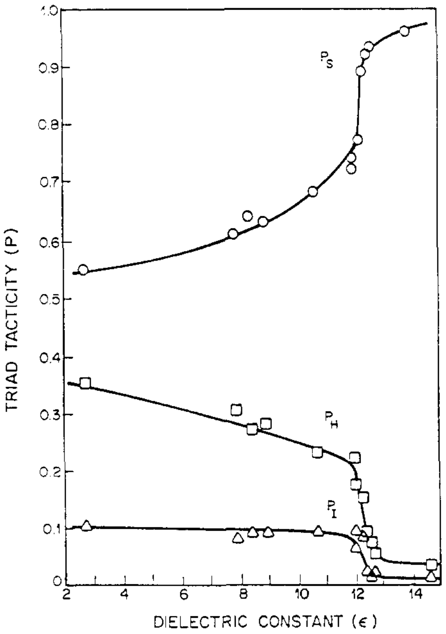

Figure 1. Triad tacticity as a function of dielectric constant for the polymerization of *p*-chloro-α-methylstyrene in methylene chloride–hexane mixtures.

A similar effect of solvent dielectric constant on reaction behavior was noted by Higashimura and co-workers[14] for the cationic polymerization of styrene initiated by tri-

Table III
Tacticity Sequence Lengths in Polymers Obtained from the Cationic Polymerization of *p*-Chloro-α-methylstyrene in Solvent Mixtures of Different Dielectric Constants

	polym tacticities				calcd sequence lengths			
	syndio		iso		iso	syndio		
reactn no.	$p(\mathrm{S})^a$	$P_\mathrm{S}{}^b$	$p(\mathrm{I})^a$	$P_\mathrm{I}{}^b$	$\mu(\mathrm{I})$	$\mu(\mathrm{S})$	ϵ^c	solvent mixture^d
1	0.96	0.92	0.04	0.01	1.0	32	14.8	A
3	0.96	0.93	0.04	0.02	1.3	48	12.5	A
4	0.96	0.92	0.04	0.01	1.0	32	12.2	A
6	0.84	0.77	0.16	0.08	2.3	10	12.1	A
7	0.83	0.72	0.17	0.06	1.5	7.5	11.9	A
9	0.80	0.68	0.20	0.09	1.6	7.3	10.6	A
11	0.78	0.64	0.22	0.09	1.6	6.0	8.4	A
13	0.72	0.55	0.28	0.10	1.6	4.0	2.8	A
15	0.96	0.91	0.04	0	0.8	24	14.8	B
16	0.94	0.89	0.06	0	1.2	16	14.6	B
17	0.94	0.87	0.06	0	0.8	16	12.7	B
18	0.92	0.85	0.08	0	1.1	12	9.9	B
19	0.88	0.79	0.12	0.03	1.3	9.9	4.2	B
20	0.84	0.73	0.16	0.04	1.4	7.0	3.2	B

[a] Diads. [b] Triads. [c] Calculated dielectric constant of solvent mixture. [d] A, methylene chloride–hexane mixture; B, methylene chloride–toluene mixture.

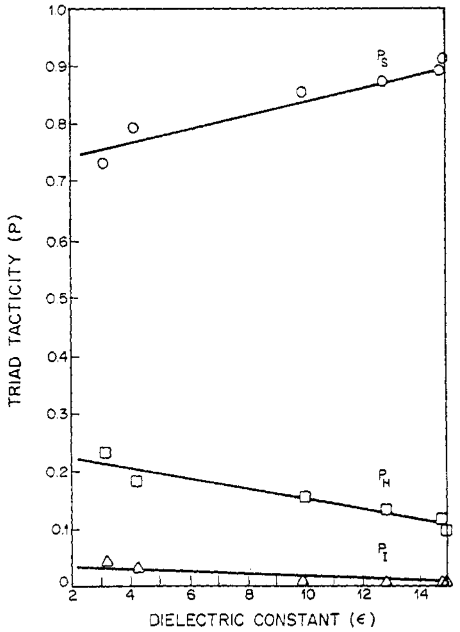

Figure 2. Triad tacticity as a function of dielectric constant for the polymerization of *p*-chloro-α-methylstyrene in methylene chloride–toluene solvent mixtures.

fluoromethanesulfonic acid at 0 °C. In that work the polymerization rate was measured in various mixtures of hexane, methylene chloride, and nitrobenzene, and their results also showed a dramatic change in the rate of polymerization above a dielectric constant of approximately 10. Such an increase could have been caused by a change in reaction mechanism from one involving contact ion pairs, or even covalent species, to one with solvated or free ions with increasing solvent dielectric constant. Higashimura and co-workers[15] also reported large changes in reaction rates for the boron trifluoride etherate initiated polymerization of α-methylstyrene with relatively small changes in dielectric constant, which also suggested possible changes in growth mechanisms.

The changes in tacticity levels for the polymers in this study may also be expressed in terms of the average lengths of syndiotactic and isotactic sequences, $\mu(\mathrm{S})$ and $\mu(\mathrm{I})$, respectively, which can be calculated[16,17] from the observed triad values: P_I, P_H, and P_S, for the isotactic, heterotactic, and syndiotactic triads, respectively. The number-average sequence lengths of the isotactic and syndiotactic units were calculated from the following equations after converting triad values to diad values, $p(\mathrm{I})$ and $p(\mathrm{S})$ for isotactic and syndiotactic diads, respectively:

$$\mu(\mathrm{I}) = p(\mathrm{I})/(p(\mathrm{S}) - P_\mathrm{S})$$

$$\mu(\mathrm{S}) = p(\mathrm{S})/(p(\mathrm{I}) - P_\mathrm{I})$$

where $p(\mathrm{S}) = P_\mathrm{S} + {}^1/_2 P_\mathrm{H}$ and $p(\mathrm{I}) = 1 - p(\mathrm{S})$.

These calculated values of the isotactic and syndiotactic sequence lengths for selected polymers obtained by polymerization in both types of solvent mixtures are shown in Table III. It is to be expected that isotatic triads are very difficult to form because of severe steric hindrance between large phenyl groups in adjacent units of this configurational sequence.[3] As a result, the activation energy for an isotactic addition should be much greater than the activation energy for a syndiotactic addition regardless of the mechanism. These steric interactions are also responsible for the low ceiling temperatures in the polymerization of such monomers. Consistent with this explanation is the observation that the average length of isotactic sequences is less than two in Table III for all polymers regardless of polymerization conditions. That is, very few isotactic triads are present in the polymer even though fairly large amounts of heterotactic triads are formed at high hexane contents.

The observed phenomena closely follow the proposal of Kunitake and Aso. The polymers obtained in homogeneous conditions showed a smooth change in tacticities. The isotacticities did not increase greatly, as expected, because of steric factors. It is interesting that large amounts of heterotactic triads, and isotactic triads above 5%, could only be formed in heterogeneous conditions where the active ion pair is most likely influenced by the highly nonpolar polymer chain. Other workers have also observed this phenomenon of tacticity changes upon precipitation of the polymer from solution.[13]

***p*-Fluoro-α-methylstyrene.** Experimental data obtained from a similar series of polymerization reactions of *p*-fluoro-α-methylstyrene with titanium tetrachloride as the initiator in various methylene chloride–hexane mixtures are collected in Table IV. In contrast to the case of the *p*-chloro-substituted monomer with tin tetrachloride, the solvent effects on polymer tacticity were negligible. No abrupt change in the tacticity values can be seen for this series, and all of the polymers showed triad syndiotactic-

Table IV

Effect of Solvent Composition on the Cationic Polymerization of *p*-Fluoro-α-methylstyrene in Methylene Chloride–Hexane Mixtures Initiated by $TiCl_4$

	solvent comp, wt %				triad tacticity			
reactn no.	CH_2Cl_2	hexane	ϵ^a	polym yield, %	P_S	P_H	P_I	σ^b
21	100	0	14.8	30	0.92	0.08	0	0.05
22	99	1	14.7	22	0.91	0.09	0	0.06
23	94	6	14.0	34	0.90	0.10	0	0.06
24	88	12	13.2	42	0.91	0.09	0	0.06
25	82	18	12.5	20	0.90	0.10	0	0.06
26	80	20	12.2	47	0.92	0.08	0	0.05
27	77	23	11.9	4	0.92	0.08	0	0.05
28	67	33	10.6	3	0.90	0.10	0	0.06
29	54	46	8.9	12	0.90	0.10	0	0.06
30	40	60	7.1	0				
31	0	100	2.0	0				

[a] Calculated dielectric constant of solvent mixture. [b] Calculated from triads: $\sigma = P_I + {}^1/_2P_H$.

Table V

Effect of Solvent Composition on the Cationic Polymerization of *p*-Fluoro-α-methylstyrene in Methylene Chloride–Toluene Mixtures Initiated with $SnCl_4$

	solvent comp, wt %				triad tacticity			
reactn no.	CH_2Cl_2	toluene	ϵ^a	polym yield, %	P_S	P_H	P_I	σ^b
32	100	0	14.8	96	0.88	0.12	0	0.06
33	98	2	14.6	14	0.90	0.10	0	0.05
34	83	17	12.7	0.2	0.90	0.10	0	0.05
35	13	87	4.2	*c*	0.93	0.07	0	0.04
36	5	95	3.2	*c*	0.87	0.13	0	0.08

[a] Calculated dielectric constant of solvent mixture. [b] Calculated from triads: $\sigma = P_I + {}^1/_2P_H$. [c] Obtained after 1-h reaction time.

Table VI

Tacticity Sequence Lengths in Polymers Obtained from the Cationic Polymerization of *p*-Fluoro-α-methylstyrene in Solvent Mixtures of Different Dielectric Constants

	polym tacticities				calcd sequence lengths			
	syndio		iso		iso	syndio		
reactn no.	$p(S)^a$	$P_S{}^b$	$p(I)^a$	$P_I{}^b$	$\mu(I)$	$\mu(S)$	ϵ^c	solvent mixture[d]
21	0.96	0.92	0.04	0	1.0	24	14	A
22	0.96	0.91	0.04	0	0.8	24	14.7	A
24	0.95	0.90	0.04	0	0.8	24	13.2	A
25	0.95	0.90	0.05	0	1.0	19	12.4	A
27	0.96	0.92	0.04	0	1	24	11.9	A
28	0.95	0.90	0.05	0	1.0	19	10.6	A
29	0.95	0.90	0.05	0	1.0	19	8.9	A
32	0.94	0.88	0.06	0	1.0	16	14.8	B
33	0.95	0.90	0.05	0	1.0	19	14.6	B
34	0.95	0.90	0.05	0	1.0	19	12.7	B
35	0.96	0.93	0.04	0	1.3	24	4.2	B
36	0.94	0.87	0.06	0	0.8	16	3.2	B

[a] Diads. [b] Triads. [c] Calculated dielectric constants of solvent mixture. [d] A, methylene chloride–hexane mixture; B, methylene chloride–toluene mixture.

ities of 90% or more. This result was surprising because poly(*p*-fluoro-α-methylstyrene) was found to also precipitate from solution upon addition of hexane to the reaction solvent. Further studies using methylene chloride–toluene mixtures as the polymerization solvent with tin tetrachloride as initiator gave the results collected in Table V. As with the *p*-chloro polymers, no polymer was obtained for $\epsilon < 4.2$ after a reaction time of 5 min. The polymers of reactions 35 and 36 in Table V were obtained after a reaction time of 1 h. Again the tacticities remained insensitive to changes in dielectric constant of the reaction solvent, and the solutions remained homogeneous over the range of ϵ values studied.

The difference in reaction solvent effect on tacticities of the *p*-fluoro and *p*-chloro polymers may be a result of either the difference in initiators used, which determine the nature of the counterions present at the active center, or the difference in the electron-contributing or -withdrawing properties of the substituents on the active growing center. Since our previous study on the *p*-chloro monomer with $TiCl_4$ initiator showed a very similar change in tacticity with solvent polarity for mixtures of methylene chloride and heptane[3] as compared with the present study with $SnCl_4$ initiator, it is unlikely that the different solvent sensitivities of the two monomers can be related to counterion differences resulting from the use of different initiators. Also the *p*-fluoro-α-methylstyrene polymers prepared with $SnCl_4$ or $TiCl_4$ initiator in methylene chloride alone exhibited nearly identical triad tacticity levels, thereby supporting the conclusion that initiator differences do not account for the different behavior exhibited by the monomers.

Substituent effects may be important, however, The σ^+ value for a *p*-fluoro substituent is −0.07 while that of a *p*-chloro substituent is +0.11.[18] Hence, the *p*-fluoro substituent acts as an electron donor in reactions involving the development of a positive charge on the carbon atom center. Electron donation by resonance interaction would decrease the positive charge at the carbocation active center and favor free ion formation. In contrast, the chloro substituent is electron withdrawing, which would increase the positive charge at the growing carbocation center and favor the formation of solvated ion pairs. If these resonance effects occur to a significant extent, then the polymerization reaction of the *p*-chloro monomer could be much more sensitive to the environment of the carbocation active center than that of the *p*-fluoro monomer.

The values of syndiotactic and isotactic sequence lengths, as calculated from the equations above, for the fluoro-substituted series of polymers obtained in mixtures of methylene chloride and hexane or toluene are collected in Table VI. It is again clearly seen that the isotactic configuration is very difficult to form, and the average isotactic sequence length is only one for all of the polymers; that is, no units longer than diads were formed and only very few of those. The syndiotactic sequence length shows a very slight solvent effect, becoming longer with increasing solvent polarity.

Experimental Section

All polymerization reactions were carried out at −78 °C under an atmosphere of dry argon with reagents purified and dried by techniques as previously reported.[1]

Proton NMR spectra for all the polymers obtained in mixtures of methylene chloride and hexane were obtained on 10% (w/v) solutions of the polymers in *o*-dichlorobenzene at 100 °C with *p*-dioxane as the internal standard. Spectra for all the polymers obtained in mixtures of methylene chloride and toluene were obtained on 10% (w/v) solutions of the polymers in toluene-d_8 at 100 °C with *p*-dioxane as the internal standard. Triad tacticities were determined from the relative areas of the three α-methyl proton resonances.

Acknowledgment. The high-field NMR experiments were performed at the NMR Facility for Biomolecular Research located at the F. Bitter National Magnet Laboratory, M.I.T., and at the NMR Facility at the University of Massachusetts at Amherst. We are grateful to the National Science Foundation for the support of this work under Grant No. DMR 80-22273.

References and Notes

(1) Lenz, R. W.; Faullimmel, J. G.; Jonte, J. M. In "Initiation of Polymerization", Bailey, F. E., Jr., Ed.; American Chemical Society: Washington, DC, 1983; p 103.
(2) Lenz, R. W.; Sutherland, J. E.; Westfelt, L. C. *Makromol. Chem.* **1976**, *177*, 653.
(3) Lenz, R. W.; Westfelt, L. C. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2147.
(4) "CRC Handbook of Chemistry and Physics", 56th ed.; CRC Press: Boca Raton, FL, 1984.
(5) Ramey, K. C.; Statton, G. L.; Jankowski, W. C. *J. Polym. Sci., Part B* **1969**, *7*, 693.
(6) Lenz, R. W.; Regel, W.; Westfelt, L. C. *Makromol. Chem.* **1975**, *176*, 781.
(7) Kunitake, T.; Aso, C. *J. Polym. Sci., Part A-1* **1970**, *8*, 665.
(8) Szwarc, M. *Makromol. Chem.* **1965**, *89*, 44.
(9) Braun, D.; Heufer, G.; Johnson, U.; Kolbe, K. *Ber. Bunsen-Ges. Phys. Chem.* **1964**, *68*, 959.
(10) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953; p 553.
(11) Higashimura, T.; Kishiro, O. *Polym. J. (Tokyo)* **1977**, *9*, 87.
(12) Lenz, R. W.; Jonte, J. M.; Gula, D. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1985**, *26* (1).
(13) Ohsumi, Y.; Higashimura, T.; Okamura, S. *J. Polym. Sci., Part A-1* **1966**, *4*, 923.
(14) Sawamoto, M.; Masuda, T.; Higashimura, T. *Makromol. Chem.* **1976**, *177*, 2995.
(15) Imanishi, Y.; Higashimura, T.; Okamura, S. *Kobunshi Kagaku* **1960**, *17*, 236.
(16) Coleman, B. D.; Fox, T. G. *J. Polym. Sci., Part A* **1963**, *1*, 3183.
(17) Bovey, F. A. "Polymer Conformation and Configuration"; Academic Press: New York, 1969; p 41.
(18) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1957**, *79*, 1913.

Morphology of Poly(ethylene terephthalate) Fibers As Studied by Multiple-Pulse ^{1}H NMR

John R. Havens[†] **and David L. VanderHart***

Polymers Division, National Bureau of Standards, Gaithersburg, Maryland 20899.
Received August 20, 1984

ABSTRACT: Drawn poly(ethylene terephthalate) (PET) fibers annealed under various conditions are investigated by proton spin diffusion as detected through nuclear magnetic resonance. The primary objective is to study morphology on the 1–50-nm scale, the smaller dimensions of which have proved difficult to characterize for PET by conventional techniques. The spin diffusion experiment is comprised of three periods: generation of a magnetization gradient among different domains, relaxation of the gradient by diffusion for a variable time, and separate detection of the magnetization corresponding to each domain. The use of a multiple-pulse sequence permits spin diffusion to be confined to the second period, resulting in enhanced resolution among the domains. This procedure allows the magnetization decay observed during the detection period to be decomposed into three components, which are assigned to mobile noncrystalline, constrained noncrystalline, and crystalline domains. Rates of polarization redistribution among these three components are studied as a function of the diffusion time. Computer modeling is carried out in order to relate these measurements to the spatial arrangement and size of the three components. The results quantify the increase in crystallinity and in crystallite size upon annealing. Information pertaining to the structure of the noncrystalline region, the importance of noncrystalline chain orientation, and the relative surface areas of the crystallites is also presented.

Introduction

A. PET Morphology. Much of the usefulness of polymeric materials derives from the ability to modify their macroscopic properties by processing. To design the optimum treatment for a particular application requires a knowledge of chain structure on the 1–50-nm scale, a region which can strongly influence mechanical performance. In this work we characterize the local morphology of uniaxially oriented poly(ethylene terephthalate) (PET) fibers. Such fibers have important structure in the 3–15-nm regime. Previous efforts to characterize this region have been made through a variety of measurements: small-angle and wide-angle X-ray scattering,[1-7] heat of fusion,[5,8] density,[5,6,9]

[†] Present address: Raychem Corp., Menlo Park, CA 94025.