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Studies on Alternating Radical Copolymerization. Analysis of Microstructures of Styrene–Maleic Anhydride, Styrene–Acrylonitrile, and Styrene–Methyl Methacrylate Copolymers by Fluorescence Spectroscopy

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ABSTRACT: Microstructures of poly(styrene-*co*-maleic anhydride), poly(styrene-*co*-acrylonitrile), and poly(styrene-*co*-methyl methacrylate) obtained by radical copolymerizations at various monomer feeds have been characterized by fluorescence spectroscopy. The results show that the microstructure of poly(styrene-*co*-maleic anhydride) varies depending on the monomer feed composition despite the fact that the overall copolymer composition is nearly 1:1; the styrene–styrene diad fraction increases with an increase in the styrene mole fraction in the monomer feed. Poly(styrene-*co*-acrylonitrile) obtained by spontaneously initiated radical copolymerization in the presence of zinc chloride is shown to be a real 1:1 alternating copolymer. Poly(styrene-*co*-methyl methacrylate) obtained in a similar manner deviates significantly from 1:1 composition. The present study shows that fluorescence spectroscopy is a useful and sensitive method for gaining information on the microstructure of copolymers formed from aryl vinyl monomers.

Introduction

There have been extensive studies on alternating radical copolymerizations from both synthetic and mechanistic interests.[1-3] The styrene (St)–maleic anhydride (MAn) system has long been regarded as a 1:1 alternating radical copolymerization system and studied most intensively.[4-16] The mechanism for the alternating radical copolymerization of the St–MAn system has been interpreted either by the penultimate model[6-8] or by charge-transfer models involving the participation of monomer charge-transfer complex in the propagation;[9-14] however, it still remains to be clarified.

Characterizations of copolymers as 1:1 alternating copolymers have usually been done on the basis of equimolar composition over a wide range of monomer feed ratios. For example, composition data of poly(St-*co*-MAn) obtained by copolymerizations both in solvents and in bulk show that copolymer compositions are nearly equimolar when the mole fraction of MAn greater than 0.1.[8,14-16] Thus the St–MAn system has been regarded as a 1:1 alternating copolymerization system. However, the equimolar composition of copolymers does not necessarily mean that they are truly 1:1 alternating copolymers. In addition, there is a limitation in the accuracy of copolymer compositions, which have usually been determined by elemental analysis, infrared absorption spectroscopy, or chemical analysis. It is therefore necessary to distinguish real 1:1 alternating copolymers from copolymers with a statistical 1:1 composition. This distinction requires information on the microstructure of copolymers.

In spite of extensive studies on 1:1 alternating radical copolymerizations, there have been only a few studies on the microstructure of the copolymers. The monomer sequence distribution of poly(St-*co*-MAn) has been studied by ^{13}C NMR spectroscopy.[14,17-19] It has been reported that the copolymerization with an excess mole fraction of styrene results in deviation from the alternating structure when the resonance of the aromatic carbon attached to the polymer chain is considered.[18] On the contrary, more recent results based on the ^{13}C NMR methylene resonance

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indicate a strong tendency to alternation in poly(St-*co*-MAn).[14,19] It has been reported, however, that considerable uncertainty in the assignment of the chemical shifts due to overlap and tacticity difference causes the results to be unreliable.[14]

In our studies of alternating radical copolymerizations[20-27] we have reported that the 2,2′-azobis(isobutyronitrile) (AIBN) initiated radical copolymerizations of *N*-vinylcarbazole (VCZ) with fumaronitrile[20,22] and diethyl fumarate (DEF)[21,22] produce 1:1 alternating copolymers over a wide range of monomer feed compositions. These copolymers were found to exhibit only monomer fluorescence due to the carbazole chromophore:[22,28] this provided evidence for the 1:1 alternating structure. It is also known that copolymerizations of weak electron-donor monomers with electron-acceptor monomers containing a polar group, in the presence of Lewis acids or metal salts, produce 1:1 alternating copolymers. 1:1 alternating copolymers prepared by radical polymerizations in the presence of ethylaluminum sesquichloride, e.g., poly(2-vinylnaphthalene-*alt*-methyl methacrylate) and poly(styrene-*alt*-methyl methacrylate), have also been reported to show only monomer fluorescence.[29] These results suggest that examination of the fluorescence spectra of copolymers as a function of the monomer feed composition should provide information on the microstructure of copolymers.

We report here the fluorescence spectroscopy characterization of the microstructure of poly(St-*co*-MAn) obtained by the AIBN-initiated radical copolymerization. The microstructures of poly(styrene-*co*-acrylonitrile) and poly(styrene-*co*-methyl methacrylate) obtained by spontaneously initiated and AIBN-initiated radical copolymerizations, respectively, in the presence of zinc chloride are also examined.

Experimental Section

Materials. Styrene (St) (Wako Chemical Industries, Ltd., guaranteed reagent), acrylonitrile (AN) (Nakarai Chemicals, Ltd., extra pure grade), and methyl methacrylate (MMA) (Wako Chemical Industries, Ltd., extra pure grade) were washed with 5% aqueous thiosulfate and sodium hydroxide, respectively, and then dried over barium oxide and distilled at reduced pressure under nitrogen. Maleic anhydride (MAn) (Wako Chemical Industries, Ltd., guaranteed reagent) was chromatographed over silica gel, recrystallized from benzene, and then sublimed twice in vacuo immediately before use. Benzene was purified by washing with (i) concentrated sulfuric acid, (ii) dilute aqueous sodium hydroxide, and (iii) deionized water; it was then dried over calcium chloride and over metallic sodium before distillation. Tetrahydrofuran (THF) was refluxed over potassium hydroxide and distilled; it was further purified by distillation over lithium aluminum hydride.

Copolymerization. The copolymerization of St with MAn was carried out in benzene at 60 °C with 2,2′-azobis(isobutyronitrile) (AIBN) as an initiator. The total monomer concentration and the initiator concentration were 1.0 and 1.0×10^{-3} mol dm^{-3}, respectively, unless otherwise specified. The copolymerization of St with AN was carried out in toluene at 30 °C with a total monomer concentration of 5.0 mol dm^{-3}. Zinc chloride was used as a catalyst with a concentration equal to 0.5 mol equiv of AN. The copolymerization of St with MMA was carried out in benzene at 60 °C with AIBN as an initiator in the presence of zinc chloride. The concentrations of the total monomer, the initiator, and zinc chloride were 1.0, 2×10^{-3}, and 1×10^{-2} mol dm^{-3}, respectively. A polymerization solution placed in a glass tube was evacuated to 10^{-3} Torr by means of several freeze–pump–thaw cycles, sealed off, and then set in a shaking thermostat maintained at a given temperature.

The polymerization was stopped at less than 8% conversion. Poly(St-*co*-MAn) was dissolved in acetone and reprecipitated repeatedly from *n*-hexane–benzene (9:1, v/v). Poly(St-*co*-AN) and poly(St-*co*-MMA) were dissolved in acetone and reprecipitated from acidic methanol (3% HCl in vol) and then repeatedly from methanol.

Table I
Compositions, Molecular Weights, and Fluorescence Intensity Ratios of Poly(St-*co*-MAn)[a]

St mole fraction				
in monomer feed	in copolymer	$M_n \times 10^{-5}$	$M_w \times 10^{-6}$	I_{330}/I_{284}
0.12	0.47	0.92	2.3	0.08
0.24	0.47	0.82	1.5	0.08
0.36	0.49	0.87	2.2	0.17
0.50	0.49	1.4	2.4	0.19
0.64	0.49	4.9	5.1	0.19
0.78	0.51	7.7	7.4	0.24
0.84	0.52	4.4	4.9	0.33
0.84[b]	0.52	2.3	2.4	0.34
0.90	0.53	11	8.6	0.40

[a] Total monomer concentration, 1.0 mol dm^{-3} in benzene; [AIBN] = 1.0×10^{-3} mol dm^{-1}; at 60 °C. [b] [AIBN] = 8.0×10^{-3} mol dm^{-3}; other conditions, the same with *a*.

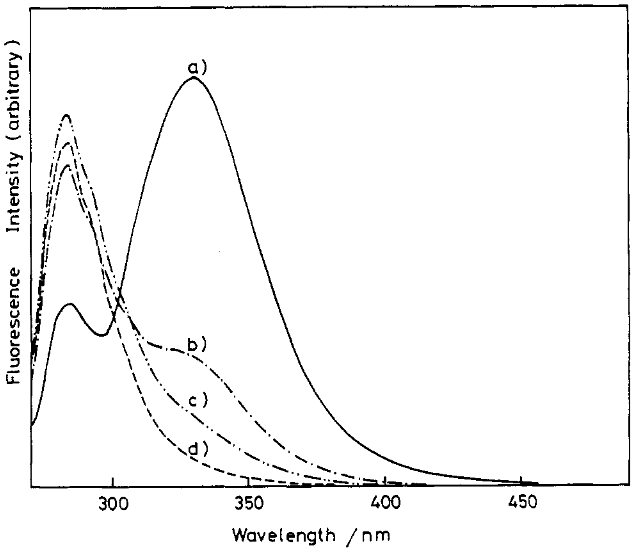
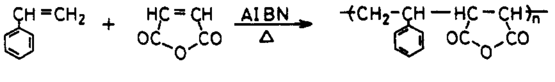


Figure 1. Fluorescence spectra of PSt and poly(St-*co*-MAn) in THF at room temperature: (a) PSt; (b–d) poly(St-*co*-MAn). Mole fraction of styrene in monomer feed: (b) 0.90; (c) 0.64; (d) 0.12.

Measurements. Copolymer compositions were determined from the carbon or nitrogen content in the elemental analysis. The fluorescence spectra of the St homopolymer and copolymers were measured in tetrahydrofuran (THF) at a concentration of ca. 2×10^{-3} mol dm^{-3} based on the St unit. The excitation wavelength was 260 nm for both the St homopolymer and the copolymers. The electronic absorption spectra and the fluorescence spectra were taken with a Hitachi U-3200 spectrophotometer and a Hitachi 850 fluorescence spectrometer, respectively. Molecular weights of the copolymers were determined by means of gel permeation chromatography with a Shimazu LC5A system using polystyrene as a standard. Care was taken to keep poly(St-*co*-MAn) in a dry condition and to use freshly prepared samples for the measurement.

Results and Discussion

Table I lists the compositions and molecular weights of poly(St-*co*-MAn) obtained at various monomer feed compositions. As is seen from Table I, the copolymer compositions are nearly equimolar over a wide range of monomer feed compositions from 0.12 to 0.9 in the St mole fraction, in accordance with literature data.[8,14-16]



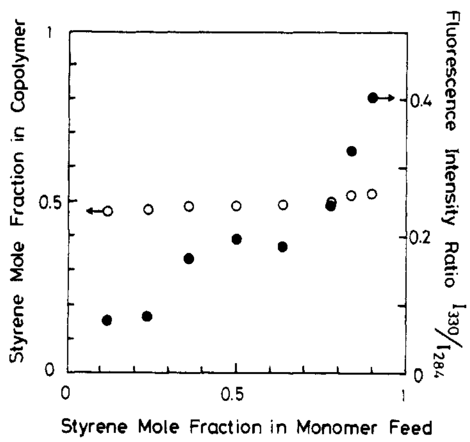


Figure 2. Compositions (○) and fluorescence intensity ratios (●), I_{330}/I_{284}, of poly(St-*co*-MAn) copolymers.

Table II
Compositions and Fluorescence Intensity Ratios of Poly(St-*co*-AN)[a]

St mole fraction		
in monomer feed	in copolymer	I_{330}/I_{284}
0.16	0.47	0.11
0.30	0.50	0.10
0.50	0.50	0.12
0.70	0.50	0.08
0.90	0.50	0.13

[a] Total monomer concentration, 5.0 mol dm^{-3} in toluene; [AN]/[ZnCl$_2$] = 2; at 30 °C.

Figure 1 shows the fluorescence spectra of a St homopolymer (PSt) prepared by radical polymerization of St and a few poly(St-*co*-MAn) obtained at different monomer feed compositions. The fluorescence spectrum of PSt shows both monomer and excimer fluorescence bands with peaks at 284 and 330 nm, respectively, as reported in the literature.[30] It is shown that poly(St-*co*-MAn) also exhibits both monomer and excimer fluorescences: the relative intensity of the excimer fluorescence to the monomer fluorescence depends on the monomer feed composition at which the copolymer is produced. The copolymer obtained at a 0.12 St mole fraction shows no distinct excimer fluorescence, exhibiting the same fluorescence as that of ethylbenzene (Figure 1d). The copolymers obtained at higher St mole fractions in the monomer feed exhibit both excimer and monomer fluorescences. The intensity of the excimer fluorescence increases with the mole fraction of St in the monomer feed (Figure 1b,c).

Figure 2 shows the ratios of the intensity of the fluorescence band at 330 nm, which is due mostly to the excimer fluorescence, to that of the monomer fluorescence band at 284 nm, for poly(St-*co*-MAn) obtained at various monomer feed compositions. The copolymer compositions are also figured. The results clearly show that whereas the copolymer compositions are nearly equimolar, the fluorescence intensity ratio, I_{330}/I_{284}, varies significantly as a function of the monomer feed composition. Molecular weights of the resulting copolymers are different from each other depending on the monomer feed compositions; however, the molecular weight does not significantly influence the fluorescence intensity ratio (Table I).

The spontaneously initiated radical copolymerization of the St–AN–ZnCl$_2$ system and the AIBN-initiated radical copolymerization of the St–MMA–ZnCl$_2$ system have been reported to produce 1:1 alternating copolymers.[31,32]

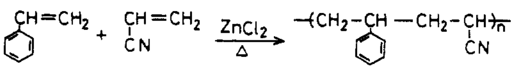
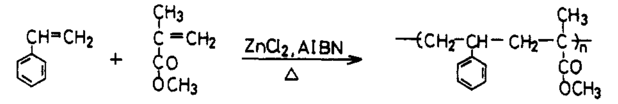


Table III
Compositions and Fluorescence Intensity Ratios of Poly(St-*co*-MMA)[a]

St mole fraction		
in monomer feed	in copolymer	I_{330}/I_{284}
0.16	0.27	0.09
0.30	0.36	0.10
0.50	0.51	0.19
0.60	0.55	0.26
0.70	0.60	0.35
0.80	0.70	0.52

[a] Total monomer concentration, 1.0 mol dm^{-3} in benzene; [ZnCl$_2$] = 1.0 × 10^{-2} mol dm^{-3}; [AIBN] = 2.0 × 10^{-3} mol dm^{-3}; at 60 °C.

Table II lists the compositions and the ratios of the fluorescence intensity, I_{330}/I_{284}, for poly(St-*co*-AN) obtained at various monomer feed compositions. The results show that poly(St-*co*-AN)s obtained at various monomer feeds have nearly 1:1 compositions and that they show almost the same fluorescence spectra consisting exclusively of the monomer fluorescence as shown in Figure 1d. On the other hand, poly(St-*co*-MMA) deviates significantly from the 1:1 composition and their fluorescence spectra exhibit both monomer and excimer fluorescences. The compositions and the intensity ratios of the fluorescence, I_{330}/I_{284}, for poly(St-*co*-MMA) are shown in Table III.



Intramolecular excimer formation in polymers has been widely observed for aryl vinyl polymers.[33] It has been shown that the intramolecular excimer formation in PSt and poly(*N*-vinylcarbazole) in a dilute solution with good solvents occurs by nearest-neighbor interactions.[28,29,34] The excimer formation by non-nearest-neighbor interactions has also been observed for certain polymers such as poly(acenaphthylene),[35] in which nearest-neighbor interactions are structurally impossible, or for certain polymers in poor solvents.[36] The head-to-head PSt has been reported to show no excimer fluorescence even in poor solvents: this strongly suggests that the excimer formation in the normal head-to-tail PSt occurs primarily between the nearest-neighboring chromophores.[37]

The fact that the fluorescence spectra of the poly(St-*co*-MAn) formed at various monomer feed compositions are different from each other in the relative intensity of the excimer to the monomer fluorescence indicates that in spite of the nearly 1:1 composition, the microstructure of the poly(St-*co*-MAn) varies depending on the monomer feed composition at which the copolymer is formed. The appearance of the intramolecular excimer fluorescence in the poly(St-*co*-MAn) indicates the existence of the St–St diad sequence as an excimer-forming site in the copolymer.

It is known that intramolecular excimer formation in vinyl aromatic polymers generally takes place via energy migration over the pendant aromatic chromophores along the polymer chain. The ratio of the excimer to the monomer fluorescence intensity (I_D/I_M) in copolymers is proportional to the product of F_{aa} times L_a as expressed in eq 1,[38] where, in the present study, F_{aa} represents a diad fraction of the St–St unit and L_a stands for the mean sequence length of the St unit. Since F_{aa} is unable to be calculated from the fluorescence spectral data, eq 1 is modified as follows. According to the Harwood equation,[39] the diad fraction F_{aa} and the mean sequence length L_a are given by eq 2 and 3, respectively, where f_a is the mole fraction (in percent) of the St unit and R is the run number in a copolymer chain. Introducing eq 2 and 3 into eq 1

Table IV
Estimation of St Mean Sequence Length of Poly(St-*co*-MAn)

St mole fraction			
in monomer feed	in copolymer	I_{330}/I_{284}	$k(L_a - 1)$
0.36	0.49	0.17	0.18
0.50	0.49	0.19	0.22
0.64	0.49	0.19	0.22
0.78	0.51	0.24	0.32
0.84	0.52	0.33	0.48
0.90	0.53	0.40	0.60

gives eq 4, which shows that I_D/I_M is proportional to the product of f_a times $L_a - 1$. By introducing the experimental data of I_D/I_M and f_a, information on the mean sequence length of the St unit, L_a, can be obtained.

$$I_D/I_M = kF_{aa}L_a \tag{1}$$

$$F_{aa} = f_a - R/2 \tag{2}$$

$$L_a = 2f_a/R \tag{3}$$

$$I_D/I_M = kf_a(L_a - 1) \tag{4}$$

The present result shows that I_D/I_M for the poly(St-*co*-MAn) increases with the mole fraction of St in the monomer feed in spite of the fact that f_a is nearly 0.5 for all the monomer feeds examined. Table IV lists the values of $k(L_a - 1)$ calculated from eq 4 as a function of the monomer feed compositions. In the real 1:1 alternating copolymer, the mean sequence length is equal to 1, and, hence, $L_a - 1$ in eq 4 represents the extent of the deviation in the mean sequence length from the 1:1 alternation. It is shown that the value of $k(L_a - 1)$ increases approximately two or three times as the St mole fraction in the monomer feed increases. The results indicate that the mean sequence length of the St unit in the copolymer increases with increasing St mole fraction in the monomer feed. The increase in the mean sequence length of the St unit in the copolymer indicates that the relative proportion of the St–St diad fraction or the St–St–St triad fraction is increased. That is, while the copolymers produced at low St mole fractions in the monomer feed contain mostly the St unit as an isolated sequence, the copolymers tend to contain increasingly the St–St diad sequence with increasing St content in the monomer feed to the extent that the increase in the St–St diad fraction F_{aa} does not significantly affect the copolymer composition f_a. The increase in the proportion of F_{aa} and hence the increase in the proportion of $L_a - 1$ with increasng St mole fraction in the monomer feed bring about more significant variation in I_D/I_M, which is proportional to the product of F_{aa} times L_a or f_a times $L_a - 1$.

It is concluded that although there is a tendency of 1:1 alternation in poly(St-*co*-MAn), the microstructure of poly(St-*co*-MAn) varies depending on the monomer feed composition. The St–St diad fraction and hence the mean sequence length of the St unit increase with the St mole fraction in the monomer feed. The real 1:1 alternating copolymer of St with MAn is not produced even at the monomer feed composition of 1:1.

In contrast to poly(St-*co*-MAn), poly(St-*co*-AN) prepared by the spontaneously initiated radical copolymerization in the presence of zinc chloride is shown to be of 1:1 alternation over a wide range of monomer feeds. The present result of the characterization of the poly(St-*co*-AN) by fluorescence spectroscopy is in accord with that by a ^{13}C NMR technique.[40] The AIBN-initiated radical copolymerization of the St–MMA–$ZnCl_2$ system, on the other hand, is shown to produce copolymers that deviate significantly from the 1:1 alternation. The difference in the compositions of the resulting copolymers between the St–AN–$ZnCl_2$ and St–MMA–$ZnCl_2$ radical copolymerization systems may be due to the complexing ability of $ZnCl_2$ being reportedly much higher for nitriles than for esters.[41]

The characterization of copolymers by fluorescence spectroscopy needs only a few milligrams of samples for the measurement and provides useful information on the monomer sequence length of copolymers with aryl vinyl monomers as one component.

Conclusion

In the present study, the fluorescence spectra of poly(St-*co*-MAn) produced by the AIBN-initiated radical copolymerization and of poly(St-*co*-AN) and poly(St-*co*-MMA) obtained by spontaneously initiated and AIBN-initiated radical copolymerizations in the presence of $ZnCl_2$, respectively, were measured as a function of the monomer feed composition in order to gain an insight into the microstructure of the copolymers. It is concluded that the poly(St-*co*-MAn) is not a real 1:1 alternating copolymer in spite of the nearly 1:1 composition over a wide range of monomer feed compositions: the St–St diad fraction increases with the St mole fraction in the monomer feed. It is also shown that the poly(St-*co*-AN) obtained in the presence of $ZnCl_2$ is a real 1:1 alternating copolymer but that poly(St-*co*-MMA) obtained in the presence of $ZnCl_2$ deviates significantly from the 1:1 alternation.

The fluorescence spectroscopy characterization is a useful and sensitive method for gaining information on the microstructure of copolymers. The method can be applied to other copolymers with aryl vinyl monomers as one component.

Registry No. (St)(MAn) (copolymer), 9011-13-6; (St)(An) (alternating copolymer), 106972-32-1; (St)(MMA) (copolymer), 25034-86-0.

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^{13}C Spin–Lattice Relaxation and Chain Local Motions of Poly(β-hydroxybutyrate) in Tetrachloroethane Solution

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ABSTRACT: Carbon-13 spin–lattice relaxation times and NOE factors were measured as a function of temperature in two magnetic fields for poly(β-hydroxybutyrate) in 1,1,2,2-tetrachloroethane-d_2. The relaxation data were interpreted in terms of chain segmental motion and methyl internal rotation by using the sharp cutoff model of Jones and Stockmayer (JS) and the Hall–Weber–Helfand (HWH) correlation function. Both models describe in a satisfactory and comparable manner the chain local motions of PHB resulting in approximately similar correlation times (1×10^{-10} s at 20 °C) and activation energy (22 kJ/mol) for cooperative segmental motions in the chain. They differ, however, in the time scale of methyl motion, which was found to be about 3–4 times faster with the JS description as compared to that using the HWH model, although both models give a comparable activation energy for methyl rotation. The latter motion is relatively fast and comparable to that observed in small and medium sized molecules in solution. The present results indicate that type 2 short-range motion, according to Helfand's terminology, is likely to occur in the PHB chain.

Introduction

Determination of ^{13}C relaxation parameters has proven to be a very powerful tool for elucidating the nature of local motions of polymer chains in solution. A number of models have been developed[1] for interpretation of nuclear spin relaxation data. Among these, the three-bond jump model of Jones and Stockmayer[2] (JS) and that of Hall, Weber, and Helfand[3,4] (HWH) have proven to be successful in describing polymer dynamics in solution. Both models will be used to describe the segmental mobility of a high molecular weight sample of the optically active poly(β-hydroxybutyrate), PHB (1), in 1,1,2,2-tetrachloroethane-d_2

$$[\text{—OCH(CH}_3\text{)CH}_2\text{C(=O)—}]_n$$

1

(TCE) solvent. On the basis of the present relaxation data, comparison of the two models will be made as well in terms of their ability to describe local motions in the PHB chain.

Experimental Section

The PHB sample used in this study was obtained from ICI Agricultural Division, Billingham, U.K. The weight-average molecular weight of the PHB sample (M_w = 400 000 g/mol) was determined by the relation[5]

$$[\eta] = 7.7 \times 10^{-5} M_w^{0.82} \qquad (1)$$

where $[\eta]$ is the intrinsic viscosity in chloroform at 30 °C. The latter quantity of PHB in TCE solution was determined by using a Cannon-Ubbelohde type dilution viscometer. The intrinsic viscosity and Huggins constant, k', in eq 2 were found to be 0.685

$$\eta_{sp}/c = [\eta] + k'[\eta]^2 c \qquad (2)$$

dL/g and 1.72, respectively. ^{13}C nuclear magnetic resonance experiments were conducted on Varian XL-200 and XL-300 spectrometers operating at 50.3 and 75.4 MHz for the carbon nucleus. The temperature was controlled to within ±0.1 °C by means of a precalibrated copper–constantan thermocouple in the probe insert. The relaxation times were measured by the standard inversion recovery technique with a repetition time longer than $5T_1$. A total of 100–200 acquisitions were accumulated for each set of 11–15 "arrayed" τ values. Values of T_1 were determined by a three-parameter nonlinear procedure with a rms error of ±5% or better. The experiments were repeated until reproducibility of the data was better than ±5%. ^{13}C NOE experiments were carried out by gated decoupling, at least three experiments being performed for each temperature value. Delays of at least 10 times the longest T_1 were used between 90° pulses. Samples of PHB, 6% (w/v) in TCE-d_2, were degassed by bubbling with nitrogen gas for 2 min before use. Nevertheless, measurements with undegassed samples did not show any measurable change in the T_1 and NOE values relative to those of degassed samples.

Results and Discussion

Table I summarizes the ^{13}C T_1 values and NOE factors for the protonated carbons of PHB as a function of temperature in two magnetic fields. As can be seen in Figure 1, the T_1 values of the backbone carbons change monotonically in both fields over the whole temperature range measured and they increase with increasing magnetic field.

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