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Mobility of Spin Probes in Nylon Films. 2. Anionic Spin Probes

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ABSTRACT: The mobility of anionic spin probes in dried nylon films was investigated by means of electron spin resonance (ESR) measurements. The effects of methylene chain length and drawing of the nylon were focused on. The mobility of the spin probes increased with increasing methylene chain length of the nylon, suggesting that the mobility of the nylon chain molecule increased with an increase in the number of methylene groups of the nylon. In the Arrhenius plots of the rotational correlation times, two or three crossover points were defined within the temperature range examined. The spin probe containing a carboxylate group (ASPI), in the nylons having 10 and 11 methylene groups in their repeating units (NY-11 and NY-12), gave three crossover points. These three crossover points, progressing from low temperature to high temperature, can be assigned to (a) the temperature where rotation around a single bond (or around an axis between the negative charge of the spin probe and the positively charged amino end groups of the chain molecules) occurs with cooperative fluctuation of the end methylene chains (T_n'), (b) the temperature at which the rotation of the spin probes becomes coupled with the rotation of the end methylene chains, including the amino groups (T_n), and (c) the temperature at which the free isotropic rotation of the probe molecules themselves occurs (T_n''), respectively. The existence of T_n'' for ASPI in NY-11 or NY-12 is attributed to the weak electrostatic interaction in the systems. The activation energy for rotation determined from the Arrhenius plots decreased with increasing methylene chain length of the nylon. This indicates that the increase of the methylene chain length makes the rotational movement of the end methylene chains easier. The effects of drawing on the mobility of the anionic spin probes were very small; i.e., the mobility of the end methylene groups was hardly affected by drawing.

Introduction

We have investigated the mobility of spin probes in nylon films by means of electron spin resonance (ESR) measurements.[1-4] The mobility was strongly affected by water in the nylon films,[2,3] by drawing of the nylon films,[4] and by the methylene chain length of the nylons.[4] In these studies we focused our attention on the interactions between the spin probes and the nylon chains and explained the above-mentioned effects on the basis of these interactions. Many investigators, however, have discussed the mobility of spin probes in relation to the mobility of polymers without considering interactions. Kumler and Boyer[5] and Törmälä et al.[6,7] discussed the correlation of the glass transition temperature, T_g, with T_{50G}, the temperature at which the extrema separation of ESR spectra becomes 5 mT (50 G). Kusumoto et al.[8] and Bullock et al.[9] interpreted these relations by using Bueche's free volume theory[10] and evaluated the segmental volume of the polymer concerned in the motions. Recently Hlouskova et al.[11] analyzed the T_g–T_{50G} relations for cross-linked isotropic polypropylene by considering the shapes of spin probes. Miles et al.[12] and Noël et al.[13] also evaluated the segmental volumes of poly(vinyl acetate) and poly(vinylidene fluoride), respectively, by using these relations. These relations are thought to be applicable to systems where the spin probe–polymer interaction is rather weak. On the other hand, the interaction between the spin probes and the nylon chains can hardly be neglected, as was pointed out in our previous papers.[2-4] Our results could not be explained by these analyses.

In the present work the mobility of anionic spin probes, which are expected to interact electrostatically with the

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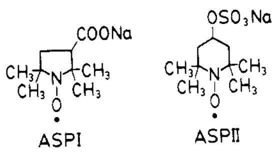

Figure 1. Anionic spin probes used.

charged amino end groups of the nylon, was investigated by means of ESR measurements. Studies of the mobility of ionic spin probes in synthetic polymer membranes have not yet appeared in the literature. Ionic spin probes have been used in investigations of micelles,[14,15] bilayers,[16] and silica gels;[17] in these investigations the interactions between charged groups in the matrices and probe molecules are discussed. The effects of drawing, of the methylene chain length in the nylon, and of the negative charge in the spin probes are discussed, taking into consideration the electrostatic interaction between the anionic spin probes and the positively charged terminal amino groups.

Experimental Section

Two anionic spin probes, sodium 2,2,5,5-tetramethyl-1-pyrrolidinyloxy-3-carboxylate (ASPI) and sodium 2,2,6,6-tetramethyl-1-piperidinyloxy-4-sulfate (ASPII), shown in Figure 1 were used. ASPI was prepared by treating 2,2,5,5-tetramethyl-1-pyrrolidinyloxy-3-carboxylic acid (Eastman Kodak Co.) with the molar equivalent of NaOH in water. The preparation of ASPII was described in our previous paper.[3] Five nylon films were used. Undrawn nylon 4 film (NY-4) was prepared by casting from formic acid solution of nylon 4 powder synthesized by a conventional method. Biaxially drawn nylon 6 film (NY-6(2D)) and undrawn nylon 6 film (NY-6(ND)) were kindly supplied by Unitika Co. Nylon 11 film (NY-11) and nylon 12 film (NY-12), both drawn by inflation, were kindly supplied by Daicell Co. The treatments of the nylon films were carried out as reported in our previous papers.[4] The amounts of amino end groups were determined as (2–4) × 10^{-5} equiv/g of nylon for all the nylons.

The spin probes were sorbed by the nylon films from aqueous solution at 343 K for 2 days. The amounts of the spin probes sorbed were about 3 × 10^{-6} mol/g of nylon for all nylon films and spin probes. This value is about 10% of the amounts of the amino end groups of the nylons. Under the sorption conditions used here, the amino end groups are thought to be positively charged so that the anionic spin probes interact electrostatically with them. All samples were dried in vacuo at 393 K for 1 day and put into an ESR tube that was sealed in the presence of air. ESR spectra were measured under the same conditions as described in our previous papers.[2-4]

Results and Discussion

Location of Anionic Spin Probes in Nylon Films. At neutral pH values in aqueous media, nylons probably exist in a zwitterion form; i.e., both carboxyl and amino groups are ionized. Under these conditions the anionic spin probes are expected to be sorbed into the nylon films under the influence of electrostatic forces, leading perhaps in some cases to the formation of contact ion pairs with the positively charged amino end groups. However, the strength of the electrostatic interactions is probably different for different anionic groups. Sulfate groups will probably interact more strongly than carboxylate groups, because sulfate groups are strong electrolytes and highly ionized[18] in the contact ion pairs, while carboxylate groups are weak electrolytes and only slightly ionized[18] in the contact ion pairs. In addition, the terminal carboxylate groups of the nylon compete with the anionic probe molecules for electrical neutralization of the cationic "sites" of the amino end groups. This competition should affect the spin probe containing a carboxylate group more strongly, since this group is the same as the terminal carboxylate group of the nylon. Thus the sulfate and carboxylate groups can be expected to behave in a different manner in the nylon films.

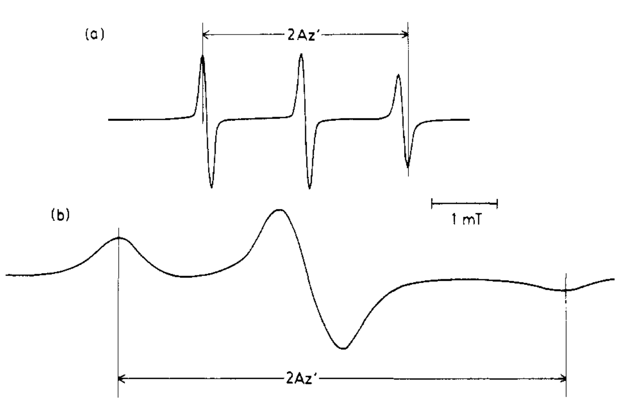

Figure 2. ESR spectra of ASPI in NY-12: (a) 444 K; (b) 129 K.

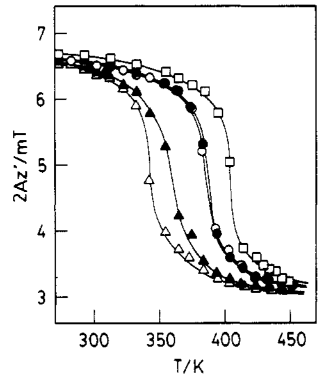

Figure 3. 2Az' vs. temperature for ASPI: (□) NY-4; (●) NY-6(2D); (○) NY-6(ND); (▲) NY -11; (△) NY-12.

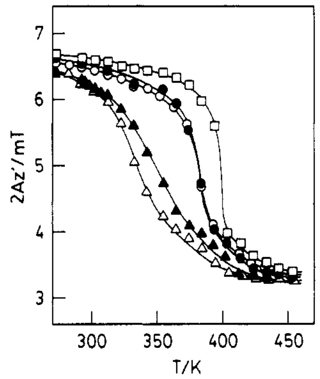

Figure 4. 2Az' vs. temperature for ASPII: (□) NY-4; (●) NY-6(2D); (○) NY-6(ND); (▲) NY-11; (△) NY-12.

The nylon films used here are dried, so the state of the terminal groups is probably different from that in wet films. Most of the water is thought to be located around the terminal groups, as pointed out in our previous paper,[3] and a higher dielectric constant in the vicinity of the end groups is expected. As the water content of the nylon films decreases, the dielectric constant decreases so that the electrostatic interaction between oppositely charged groups is strengthened. From this, it is concluded that the electrostatic interaction between the anionic spin probes and the positively charged amino end groups is maintained and may even be stronger in the dried nylon films.

Extrema Separation. As shown in Figure 2, broad and sharp three-line spectra were observed in the low- and high-temperature regions, respectively. The extrema separation of the ESR spectra, 2Az' in the figure, which is a measure of the mobility of the spin probes, decreases

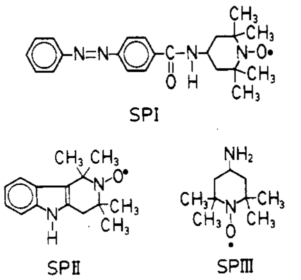

Figure 5. Nonionic spin probes.

Table I
T_{50G} (K)

	NY-4	NY-6(2D)	NY-6(ND)	NY-11	NY-12
ASPI	406	388	385	358	340
ASPII	398	381	382	348	334
SPI[a]	424	408	404	388	376
SPII[a]	428	414	414	388	385
SPIII[a]	416	391	365	360	361
T_g[b]	373	358	318	340	331

[a] Cf. ref 4. [b] Determined by dynamic mechanical measurement at 10 Hz.

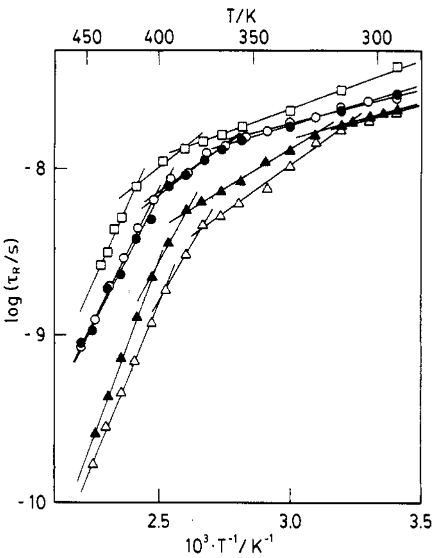

Figure 6. Arrhenius plots of τ_R for ASPI: (□) NY-4; (●) NY-6(2D); (○) NY-6(ND); (▲) NY-11; (△) NY-12.

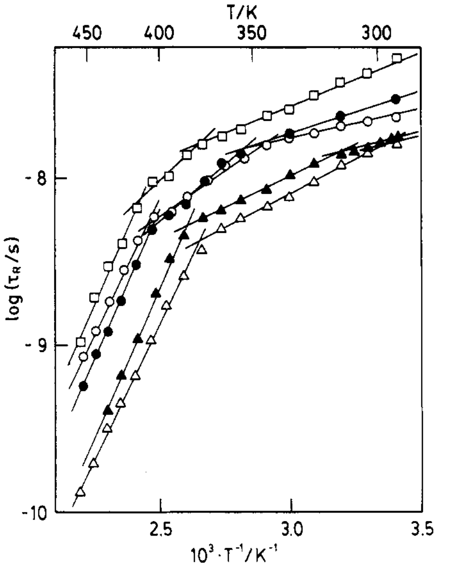

Figure 7. Arrhenius plots of τ_R for ASPII: (□) NY-4 (●) NY-6(2D); (○) NY-6(ND); (▲) NY-11; (△) NY-12.

with increasing mobility. In all the systems 2Az′ decreased with increasing temperature (Figures 3 and 4); i.e., the mobility of the spin probes increased with increasing temperature. However, the shapes of the curves of 2Az′ against temperature vary from system to system. For ASPI, the shapes of the curves did not change with methylene chain length and drawing of the nylons, and 2Az′ decreased steeply in a certain temperature region. For ASPII, on the other hand, the change became more gentle with an increase in the number of methylene groups in the nylon repeat unit. This suggests that the spin probe containing a sulfate group monitors the mobility of the end methylene groups of the nylons more clearly than the spin probe containing a carboxylate group. The effects of drawing on the shapes of the curves were very small for the anionic spin probes. The shapes are determined by the changes of the rotational correlation times τ_R with temperature; a detailed discussion is given in the next section.

T_{50G}, at which 2Az′ becomes 5 mT (50 G), was determined from Figures 3 and 4 and is given in Table I. T_{50G} for ASPI and ASPII, as for the nonionic spin probes SPI, SPII, and SPIII (Figure 5), decreased in the order NY-4 > NY-6(2D) ≥ NY-6(ND) > NY-11 > NY-12. Though T_{50G} has been correlated empirically with the glass transition temperature, T_g,[5-9] T_{50G} reflects not only the mobility of the polymer chains but also the structures of the spin probes and the interactions between the polymer chains and the probe molecules, as was reported in our previous papers.[2-4] The above fact is one of the reasons T_{50G} is quite different from T_g determined by means of dynamic mechanical measurement at 10 Hz. Another reason is that T_g increases with increasing frequency, i.e., the frequency for T_{50G} (10^8 Hz) is much larger than that for T_g (10 Hz). However, an essential reason is that T_g reflects the macroscopic character of the segmental mobility of polymers, while T_{50G} reflects the microenviroment around the probe molecules, i.e ., T_{50G} is dependent on the location of the spin probes. The T_{50G} values for SPI, SPII, and SPIII were larger than those for ASPI and ASPII (Table I). The anionic spin probes are belived to interact electrostatically with the positively charged amino end groups and to give information about the mobility of the end methylene chains. On the other hand, the nonionic spin probes are thought to be located in the more hydrophobic regions[4] and to monitor the mobility of the polymer chains that exist in those regions. SPIII appears to form a hydrogen-bonded cross-link between two amido groups of the nylon in the drawn nylon films. From the above results, it is concluded that T_{50G} is dependent on the location of the spin probes in the polymer matrices and on the interactions between the spin probes and the polymer chains.

Rotational Correlation Times. Rotational correlation times τ_R were determined from the ESR spectra. As was reported in our previous papers,[2-4] the equations derived by Kivelson [19] and Kuznetsov et al.[20] were used for the calculation of τ_R. τ_R used here was determined with the assumption of isotropic rotation, and it should be termed the "apparent rotational correlation time".

The Arrhenius plots of τ_R are shown in Figures 6 and 7. Under the assumption that the plot is divided into two or three straight lines, the calculation for the individual cases is repeated by the least-squares method until a correlation coefficient in each region is greater than 0.98. In the case of NY-4, which has a limited amount of data in the medium-temperature region, the correlation coefficient was set as 0.95. For rigorous analysis, the method proposed by Boyer et al.[21] should be used, but the basis

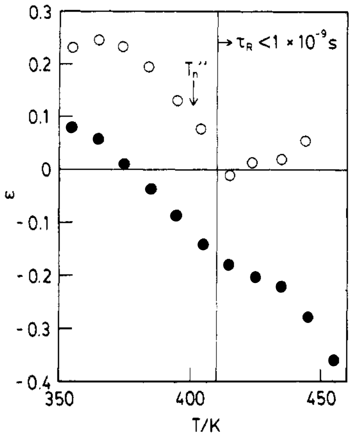

Figure 8. ε vs. temperature for NY-12: (○) ASPI; (●) ASPII.

of the procedure used here is essentially the same as their analytical method. For ASPI in NY-11 and NY-12, three crossover points were defined, but only two were defined for all of the other systems. The crossover points in the low- and high-temperature regions are designated T_n' and T_n, respectively. The crossover point in the higher temperature region, defined only for ASPI in NY-11 and NY-12, is designated T_n''. However, it is difficult to recognize whether T_n'' exists or not from only the Arrhenius plots of τ_R. Here it is worthwhile to mention the rotational anisotropy. As was described in our previous paper,[4] the rotational anisotropy can be characterized by the parameter ε. ε reflects only the anisotropy of motion in the region of $\tau_R < 1 \times 10^{-9}$ s, but it also includes the mobility of the probe molecules in the region of $\tau_R > 1 \times 10^{-9}$ s, so that ε in this latter region cannot be used for this discussion. ε equals zero for isotropic rotation, and it becomes negative for rotation around the x axis corresponding to the N–O bond direction.[22] The change of ε with temperature for NY-12 is shown in Figure 8. For ASPII, and for $\tau_R < 1 \times 10^{-9}$, ε was negative for all the nylon films, indicating anisotropic rotation around the x axis. On the other hand, in the case of ASPI ε was positive for NY-4, NY-6(2D), and NY-6(ND) within the temperature range measured, while it approached zero for NY-11 and NY-12 above T_n''. This suggests that ASPI rotates freely and isotropically without any specific bonding restrictions above T_n''. This fact clearly supports the existence of T_n''.

The motional modes in the individual temperature ranges may be explained as follows. Full rotation around a single bond in the spin probes, or around the axis between oppositely charged groups, is though to start at T_n' (Figure 9a). At the same time the end methylene chains probably start to fluctuate. T_n is assumed to correspond to the temperature at which the rotation of the spin probes becomes coupled with the rotation of the end methylene chains, including the amino groups (Figure 9b). As described above, at T_n'' the electrostatic interaction between the negatively charged spin probes and the positively charged amino end groups may become less directional, and consequently the probe molecules may start to rotate freely (Figure 9c). T_n', T_n, and T_n'' aree shown in Table II.

T_n' decreased in the order NY-4 > NY-6(2D) > NY-6(ND) > NY-11 > NY-12. This suggests that the increase of the methylene chain length makes it easier for the end methylene chains to fluctuate, resulting in easier rotation around a single bond in the probe molecules or around the axis between the oppositely charged groups. The difference in T_n' between drawn and undrawn films was rather small for the anionic spin probes, suggesting that the mobilities of the end groups are hardly affected by drawing. When the T_n' values for ASPI are compared with those for SPI and SPIII, for which rotation around a single bond was observed,[4] the change of the values for the spin probes varies from nylon to nylon. T_n' decreased in the order SPI > SPIII > ASPI > ASPII for NY-6(2D), NY-11, and NY-12, in the order SPI > ASPI > SPIII > ASPII for NY-6(ND), and in the order ASPI ~ SPI ~ ASPII > SPIII for NY-4. This result is presumably explained as follows. Long methylene end chains are more flexible, so that the anionic spin probes bound near them can move more freely than those nonionic spin probes bound to the amido groups of the main chains. On the other hand, the shorter end methylene chains are less flexible, resulting in similar T_n' values for both the anionic and the nonionic probes. T_n' for SPIII is strongly affected not only by the methylene chain length but also by drawing.[4] Hence in the case of SPIII the effects of drawing should be considered.

T_n also decreased with increasing methylene chain length of the nylon. Here it is necessary to mention that T_n for the nonionic spin probes is believed to correspond to the temperature at which the free rotational motion of the whole probe molecule occurs, while T_n for the anionic probes appears to correspond to temperature at which the rotation of the spin probes becomes coupled with the

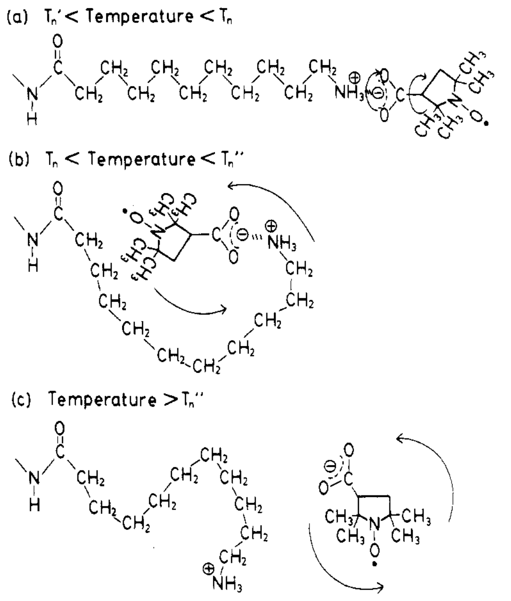

Figure 9. Model of the interaction between the anionic spin probes and the positively charged amino end groups of the nylon.

Table II
T_n', T_n, and T_n'' (K)

	NY-4	NY-6(2D)	NY-6(ND)	NY-11	NY-12
			T_n'		
ASPI	384	364	355	324	312
ASPII	378	351	342	321	292
SPI[a]	381	371	362	354	336
SPIII[a]	366	365	347	333	332
			T_n		
ASPI	414	401	403	388	377
ASPII	413	403	409	380	374
SPI[a]	441	423	425	403	389
SPII[a]	412	394	399	383	374
SPIII[a]			403	379	380
			T_n''		
ASPI				402	401

[a] Cf. ref 4.

Table III
E_a^R (kJ•mol^{-1})

	NY-4	NY-6(2D)	NY-6(ND)	NY-11	NY-12
			ASPI		
low	10.4 ± 0.3	8.9 ± 0.2	6.90 ± 0.12	7.77 ± 0.17	8.0 ± 0.3
medium	24.1 ± 0.7	25 ± 3	21 ± 2	20.9 ± 1.7	23.0 ± 1.0
high	67 ± 3	60 ± 3	62.0 ± 1.3	56 ± 2	57 ± 3
very high				81.6 ± 1.3	69.3 ± 1.9
			ASPII		
low	11.9 ± 0.4	7.5 ± 0.2	5.11 ± 0.10	7.5 ± 0.4	7.5 ± 0.4
medium	29 ± 6	27 ± 4	20.5 ± 1.5	15.0 ± 1.8	15.1 ± 0.7
high	70 ± 5	66.3 ± 1.0	62.5 ± 0.7	61 ± 6	59.8 ± 1.5

motions of the end methylene chains while maintaining the electrostatic interaction. Therefore in the case of the anionic probe molecules the molar volumes including the end methylene chain should be taken into account. T_n for SPI was higher than for the other four spin probes, which had almost the same T_n values. This result may be explained in terms of the molar volumes and the interactions between the spin probes and the nylon chains. The molar volume of SPII is larger than that of SPIII, but SPII does not interact with the nylon chains so strongly as SPIII, which has an amino group capable of forming hydrogen bonds with nylon. As a result of these effects, SPII and SPIII have similar T_n values. Because the anionic spin probes have large unit motional volumes and their motions are restricted by the linkage to the main chains, their T_n values are thought to be similar to those of SPII and SPIII. On the other hand, SPI has a large molar volume and can interact with the nylon chains through hydrogen bonds, consequently leading to the higher T_n value for this probe.

The appearance of T_n'' seems to be dependent on the strength of the interaction. From this point of view, it is thought that a carboxylate group interacts with the amino end groups more weakly than a sulfate group, and as a result it is easier to break the electrostatic interaction between the negatively charged carboxylate groups and the positively charged amino end groups. Furthermore, the long methylene chain can move so vigorously that the electrostatic bond breaks more easily. For these reasons, T_n'' could be observed only for ASPI in NY-11 and NY-12.

The activation energies for rotation, E_a^R, determined from Figures 6 and 7 are given in Table III. Although τ_R values below 293 K are not shown in these figures, they were used to determine E_a^R in the low-temperature region below T_n'. E_a^R in the low-temperature region was of the same order as for the nonionic spin probes[4] and for other polymer–spin probe systems.[23] The spin probes probably undergo rotational vibrations only in this region. The decrease of E_a^R with increasing methylene chain length in this region may be due to the flexibility of the end methylene chain. In the medium-temperature region between T_n' and T_n, E_a^R for ASPI was scarcely dependent on the methylene chain length, while E_a^R for ASPII decreased with an increase in the number of methylene groups. From this, it is thought that for ASPI the rotation around the axis between the oppositely charged groups (Figure 9a) takes place more easily, and the activation energy for this rotation is observed, while for ASPII it is though to be difficult for this rotation to occur, and the activation energy for the fluctuation of the end methylene chains is monitored. The longer the methylene chains, the easier the fluctuation of the end methylene chains. Also, drawing makes the fluctation more difficult.

E_a^R in the high-temperature region between T_n and T_n'' decreased with increasing methylene chain length. This result is opposite to that for SPII and SPIII, whose E_a^R increased with an increase in the methylene chain length.[4] The change of E_a^R for the nonionic spin probes was discussed by considering the jumping distance of the translational diffusion.[4] The anionic spin probes, however, are not believed to diffuse translationally in this temperature region, owing to the electrostatic restriction. Therefore the motional flexibility of the end methylene chains is probably one of the main factors in determining E_a^R. For this reason, the long methylene chains, which can move more flexibly, give the smaller activation energy. E_a^R in the very high temperature region above T_n'' was very large, suggesting that it includes the energy required to break the electrostatic bonds. Thus the implication of E_a^R for the anionic spin probes is very different from that for the nonionic ones.

Conclusion

On the basis of our results, we conclude that the anionic spin probes interact electrostatically with the positively charged amino end groups in nylon and monitor the mobility of the end methylene chains. The anionic spin probe containing a sulfate group (ASPIII) interacts with the amino end groups more strongly than the anionic spin probe containing a carboxylate group (ASPI) and monitors the mobility of the end groups more clearly. In ASPI/NY-11 and NY-12 systems, free isotropic rotation was observed at the highest temperatures, owing to the breaking of the electrostatic interaction. Effects of drawing were very small, suggesting that the flexibilities of the end methylene chains are hardly influenced by drawing. Thus the mobility of the spin probes is affected by the structure of the probe molecules, by the structure of the macromolecules, by the location of the probe molecules, and by the interactions between the probe molecules and the macromolecules. From this we can conclude that the use of appropriately designed spin probes makes it possible to explore the microenvironments in polymer matrices.

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Registry No. ASPI, 71259-41-1; ASPII, 105473-46-9; NY-4 (SRU), 24938-56-5; NY-4 (homopolymer), 24968-97-6; NY-6(2D), 25038-54-4; NY-11 (SRU), 25035-04-5; NY-11 (homopolymer), 25587-80-8; NY-12 (SRU), 24937-16-4; NY-12 (homopolymer), 25038-74-8.

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Molecular Weight Distribution of Reversible ARB Polymerization in Homogeneous Continuous Flow Reactors with Monomers Exhibiting Unequal Reactivity

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ABSTRACT: Reversible step-growth polymerization with unequal reactivity of monomer in homogeneous continuous flow reactors (HCSTRs) has been modeled. The resulting mole balance relations are nonlinear interacting algebraic equations that must be solved simultaneously. These have been made noninteracting under transformation, which leads to considerable saving in computation time. Subsequently the mole balance equations have been properly combined to give a moment-generating function which is a Riccatti differential equation for reversible polymerization. This reduces to an algebraic equation for irreversible polymerization, and from the moment-generating function thus found, an analytical solution of the molecular weight distribution (MWD) has been derived. The moment-generating function has been solved by splitting the Riccatti differential equation under transformation into two linear differential equations. The solution of these is in the vector Volterra form and can be represented by a Neumann series. Two terms of the series were derived and were found to describe the MWD for low conversion very well. Finally the effect of the unequal reactivity and the equilibrium ratio has been examined on the equilibrium MWD and its moments.

Introduction

Polymer formation from its monomer occurs through the presence of growth centers, and polymerization is broadly classified into chain-growth and step-growth reactions, depending upon the nature of the growth center. In step-growth polymerization, growth of polymer chains occurs through reaction of functional groups. Depending upon whether the starting monomer is bifunctional or multifunctional, the resulting polymer is either linear or branched (or network) in molecular structure. The step-growth polymerization of bifunctional monomers ARB, where A and B are reacting functional groups, can be schematically written as

$$P_n + P_m \underset{k'_{p,m+n}}{\overset{k_{p,mn}}{\rightleftharpoons}} P_{m+n} + W \qquad m, n = 1, 2, ... \qquad (1)$$

where P_m is a polymer molecule having m repeat units and W is a low molecular weight condensation product. $k_{p,mn}$ and $k'_{p,m+n}$ are respectively the rate constants for the forward and reverse reaction steps, which are in general chain-length dependent.

The forward and reverse rate constants in eq 1 are usually complex functions of chain length of the polymer molecules involved. Flory was the first to propose the equal reactivity hypothesis[7,8] based on experimental results of Bhide and Sudborough[6] on the esterification of aliphatic acids in the presence of excess ethanol. In this, $k_{p,mn}$ and $k'_{p,m+n}$ were assumed to be independent of chain lengths m and n. Under this assumption, the mole balance equations of various species collapse into one, and the overall polymerization can be represented by reaction of functional groups. Industrially, polymerization can be carried out in either batch or continuous reactors, and the analysis of these reactors for step-growth polymerization has recently been reviewed.[9-13]

Mathematical results derived from the equal reactivity hypothesis have been used to explain the gross kinetic features. Comparison with experimental data shows that the polymerization is far more complex than that represented by the equal reactivity hypothesis.[12-17] In the literature, in the reaction-controlled polymerization, the discrepancy between the two is explained by the nonequal reactivity that can arise due to either the unequal reactivity of functional groups or the chain-length-dependent reactivities in the forward and the reverse steps of eq 1. Case[14] has analyzed various situations of the former using probabilistic arguments and derived the molecular weight distribution (MWD) in terms of the conversion of functional groups. The effect of unequal reactivity was then shown to have considerable effect on the MWD of the polymer.

Nanda and Jain[17] have analyzed the case of chain-length-dependent reactivity in irreversible step-growth polymerization. They assumed the forward rate constant to be falling linearly with the chain length and derived the MWD. Recent experiments have shown that the change in the reactivity in dilute Θ-solution of functional groups with chain length is described by an S-shaped curves.[18]

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