PHOTOCROSSLINKING REACTION OF POLYDIMETHYLSILOXANE/BENZOPHENONE —CONTAINING POLYIMIDES IN SOLUTION

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The intermolecular crosslinks and the changes in polymer coil dimension during the competitive intra- and intermolecular photocrosslinking reactions were studied for polyimides of benzophenonetetracarboxylic dianhydride with oligomers having various degrees of bis(aminopropyl) polydimethylsiloxane (BAPSX, $n=8, 15, 61$) in tetrahydrofuran under u.v. irradiation at 30°C. The magnitude of $\bar{M}_w$, $\langle s^2 \rangle^{1/2}$, and A_2 was evaluated by a light-scattering measurement. The deviation of the intermolecular crosslinks from linearity during the reaction becomes more pronounced as the initial polymer concentration decreases or the number of BAPSX oligomers in a polyimides increases. The value of $\phi_{inter}/[C]_0$ for a polyimide with a BAPSX oligomer ($n=8$) was determined to be $6.7 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$ in the early stage of crosslinks formation. The extent of the contraction of polymer coils due to intramolecular crosslinking increases as the number of BAPSX oligomers in a polyimide decreases.

1. Introduction

The changes in conformation, flexibility, molecular weight, and comonomer composition of the polymers exert various effects on the reactivity of the functional polymers such as photoresist and photocromic polymers. The changes in polymer coil dimension and intermolecular crosslinking density are related to the balance in the competition between intra- and intermolecular crosslinking in solution [1-3]. Since the contraction of polymer coils occurs because of predominant intramolecular crosslinking and prevents the interpenetration of polymers, the rate for intermolecular reaction becomes smaller as the reactive groups in a polymer increases [1].

The photoreaction of polymers with reactive groups in its main chain has been studied mainly in the solid state by many reseachers [4-6].

A fully imidized, solvent-soluble polyimide system has been reported by Pfeifer and Nakano [7,8]. For example, photosensitive polyimides prepared from benzophenonetetracarboxylic dianhydride (BTDA) with an antisymmetric diamine compound is soluble in common organic solvents [7,8]. Photosensitive polyimides containing BTDA in dichloromethane behave like a flexible polymer which forms many intramolecular crosslinks during photocrosslinking.

We have recently reported the effects of BTDA contents and the number of alkyl substituents in the diamine component in the polyimide on competitive intra- and intermolecular photocrosslinking reaction in solution [3,9]. The kinetic parameters and the changes in a polymer coil dimension depend on the diamine component and the amount of BTDA in a polyimide.

In the present paper, the diamine component in a polyimide containing BTDA was replaced by bis(aminopropyl)

polydimethylsiloxane oligomers ($n=8,15,61$). The photoreactivity and the changes in polymer coil dimensions due to the intra- and intermolecular reactions were evaluated by a light-scattering measurement.

2. Experimental Procedures

A polymer was prepared from BTDA and the diamine monomer. BTDA was recrystallized from acetic anhydride and dried at 180°C in vacuum, and bis(aminoprpyl) polydimethyl siloxane oligomers (BAPSX) were supplied by Toray Dow Cowning Silicone Co., Ltd. and used as received. The procedure for the preparation of polymers as follows: BAPSX(0.01 mol) was accurately weighed into a round-bottom flask and dissolved in THF (100 ml) at room temperature. The stoichiometric amount of BTDA was added and the solution was stirred for 4 h at room temperature. For the imidization of the polyamic acid, 130 g acetic anhydride and 55 g of pyridine were added and the mixture was then heated in an oil bath at 40°C for 2 h. After cooling, the mixture was poured into ice water. The solid which precipitated was

Table 1. Characterization of polyimides

n	$\bar{M}_n$	$\bar{M}_w$	$\langle S^2 \rangle^{1/2}$ (Å)	A_2 (mol ml g ⁻²)	dn/dc (ml/g)
8	2.25×10^5	237	1.12×10^3	5.66×10^{-4}	0.0765
15	3.44×10^5	234	1.07×10^3	0.49×10^{-4}	0.0570
61	12.0×10^5	245	1.02×10^3	0.26×10^{-4}	0.0260

filtered off, washed with dilute Na₂CO₃ solution, water, and methanol, and then dried. The polymers were dissolved in THF, reprecipitated with cyclohexane, and again washed methanol, and then dried. The products are checked with i.r. spectra using a i.r. spectroscopy (Jasco IR-810 Type). The characteristics of the polyimides are given in Table 1.

The solution in a pyrex cell with a polymer concentration of 3.6-18 g dm⁻³ was irradiated by a 450 W high-pressure Hg lamp (Ushio UM-452) with a glass filter (Toshiba UV-D36A) at 30°C. Weight-average molecular weight, $\bar{M}_w$, root-mean-square radius of gyration, $\langle S^2 \rangle^{1/2}$, and the second virial coefficient, A_2 , were measured with a light-scattering photometer (Union Giken LS-601 Type) and calculated by using a personal computer attached to the photometer. Details of the determination have been given [1].

3. Results and Discussion

Changes of Intermolecular Crosslinking Density during the Reaction

The extent of intermolecular crosslinking in the competition between intra- and intermolecular processes was estimated from the change in molecular weight, measured by light-scattering. For a polyimide with BAPSX (n=8), the change in $\bar{M}_w$ against the irradiation time, t , becomes marked with increasing the initial polymer concentration as shown in Figure 1; for the experiment with $[C]_0 = 18$ g dm⁻³, the value of $\bar{M}_w/\bar{M}_{w,0}$ becomes ca 25 times

Fig. 1. Variation of $\bar{M}_w/\bar{M}_{w,0}$ of a polyimide with a BAPSX oligomer (n=8) in THF. Concentration/g dm⁻³: ●, 18; ○, 10; ◐, 3.6.

Fig. 2. Number of intermolecular crosslinks per monomer unit, formed by intermolecular photocrosslinking of a polyimide with a BAPSX oligomer ($n=8$) in THF. Concentration/ g dm^{-3} : $\bullet$, 1.8; $\circ$, 1.0; $\bullet$, 0.3.

Fig. 3. Number of intermolecular crosslinks per monomer unit, formed by intermolecular photocrosslinking of polyimides with BAPSX oligomers (n : $\circ$, 8; $\triangle$, 15; $\square$, 61) at 10 g dm^{-3} .

larger than its initial value. The change in $\bar{M}_w$ of a randomly crosslinked polymer during irradiation satisfies the following equation [10]:

$$\bar{M}_w = \bar{M}_{w,0} / (1 - 2\rho\bar{N}_{w,0}) \quad (1)$$

where ρ is the intermolecular crosslinking density, i.e., the number of crosslinks per a monomer unit, and $\bar{N}_{w,0}$ and $\bar{M}_{w,0}$ are respectively the weight-average degree of polymerization and the weight-average molecular weight of the polyimide before crosslinking. For a polymer with BAPSX ($n=8$), Figure 2 shows the plots of ρ against t . The dotted line represents the point of the theoretical onset of gelation at $\rho_g = 1/2\bar{N}_{w,0}$ for $\bar{M}_w \gg \bar{M}_{w,0}$. The values of ρ increase rapidly in the early stage of crosslink formation, becoming close to $\rho_g = 2.1 \times 10^{-3}$ in all cases. The abrupt increase in ρ becomes greater as the initial polymer concentration increases. From the slopes of the straight lines in the initial reaction in Figure 2, the quantum yield for intermolecular crosslinking, $\phi_{\text{inter}}/[C]_0$, was determined to be $6.7 \times 10^2 \text{ dm}^3 \text{ mol}^{-1}$. For polymers with BAPSX oligomers ($n=8, 15, 61$) as shown in Figure 3 at $[C]_0 = 10.0 \text{ g dm}^{-3}$, the values of ρ deviate from linearity during the crosslinking. This tendency

becomes more pronounced as the number of BAPSX oligomers in polyimides increses. These results suggest that the contraction of polymer coil caused by the intramolecular reaction or the physical entanglements is responsible for the decrease in chain interpenetration. This behavior is similar to that for a flexible polymer with pendent cinnamoyl groups [1,2].

The photocrosslinking mechanism of this benzophenone-containing polyimide has been investigated by using gel dose and other methods [4,6,11]. More recently the photoreduction mechanism of the model compounds of benzophenone-containing polyimides has been discussed based on the intramolecular CT character by Hasegawa *et al.*[12].The quantum yields of a polyimide in THF are much greater than that in dichloromethane [3,9]. Perhaps this difference is attributed to the hydrogen abstraction from THF.

From the light-scattering measurements, the values of the second virial coefficient, A_2 , are $(2.6 \times 10^{-5} - 5.7 \times 10^{-4})$ mol ml g⁻² for polyimides with BAPSX oligomers (n=8,15,61) in THF before photoirradiation. The value of A_2 becomes extremely smaller as the number of BAPSX oligomers in a polyimide increases. These values are much too small compared to the values, 2×10^{-3} mol ml g⁻², for polyimides, which are composed of BTDA and tetraethylmethylenedianiline. We obtained the changes in A_2 and $\bar{M}_w$ during photoirradiation as shown in Figure 4. The plots of A_2 against $\bar{M}_w$ display downward curvature. The change in A_2 is marked in the initial stage, suggesting that the intramolecular photocrosslinking proceeds in competition with the intermolecular process.

Change in Polymer Coil Dimension during the Reaction

The values of root-mean-square radius of gyration, $\langle s^2 \rangle^{1/2}$, are plotted on a double logarithmic scale against $\bar{M}_w$ for a polyimide with a BAPSX oligomer (n=8) in

Fig. 4. Plots of A_2 against $\bar{M}_w$ for polyimides with BAPSX oligomers (n:○,8;△,15;□,61) in THF at 10 g dm^{-3} .

Fig. 5. Molecular weight dependence of $\langle s^2 \rangle^{1/2}$ for a polyimide with a BAPSX oligomer (n=8) in THF. Concentration/g dm⁻³: ●, 18; ○, 10; ●, 3.6.

Fig. 6. Molecular weight dependence of $\langle s^2 \rangle^{1/2}$ for polyimides with BAPSX oligomers (n: ○, 8; △, 15; □, 61) at 10 g dm⁻³.

Figure 5. The plotted points give three different lines according to the initial polymer concentration. This indicates that the magnitudes of $\langle s^2 \rangle^{1/2}$ and $\bar{M}_w$ are related to the degree of competition between intra- and intermolecular crosslinking. When the concentration increases, the dimension of polymer coils increases gradually owing to the increase in molecular weight caused by the intermolecular reaction overcoming the contraction caused by the intramolecular reaction. However, the values of $\langle s^2 \rangle^{1/2}$ for $[C]_0 = 3.6$ g dm⁻³ of a polyimide with a BAPSX oligomer (n=8) are almost unchanged despite the large change of $\bar{M}_w$. This may be attributed to the accidental cancelling of the expansion due to the molecular weight increase with the contraction due to intramolecular reaction. For polyimides with BAPSX oligomers (n=8, 15, 61) at $[C]_0 = 10.0$ g dm⁻³ as shown in Figure 6, the magnitude of the dimension of polymer coils depends on the number of BAPSX oligomers in a polymer. In order to evaluate the net contraction of polymer chains due to intramolecular crosslinking, the contraction ratio, g , is given by equation (2) as in our previous analysis [1],

$$g = \langle s^2 \rangle_{c,r} / \langle s^2 \rangle_1 \quad (2)$$

where $\langle s^2 \rangle_{c,r}$ is the mean-square radius of gyration of the photoirradiated polymers given in Figures 5 and 6. The value of $\langle s^2 \rangle_1$ is that of the corresponding linear polymer having the same $\bar{M}_w$, and was calculated by using the relationship $\langle s^2 \rangle_1 \propto \bar{M}_w^{2/3(1+a)}$ where a is

Fig. 7. Plots of g against M_w for a polyimide with a BAPSX oligomer ($n=8$) in THF. Concentration/ g dm^{-3} : $\bullet$, 18; $\circ$, 10; $\circ$, 3.6.

Fig. 8. Plots of g against M_w for polyimides with BAPSX oligomers (n : $\circ$, 8; Δ , 15; $\square$, 61) in THF at 10 g dm^{-3} .

the viscosity coefficient, assumed to be 0.5. The contraction ratio, g , is plotted against M_w in Figures 7 and 8. The values of g decrease with progress of crosslinking, particularly for the initial stages of the reaction, and also more rapidly for the lower initial polymer concentration. The value of g finally approaches 0.1 for a polyimide with a BAPSX ($n=8$) at $[C]_0=3.6 \text{ g dm}^{-3}$ as shown in Figure 7. The result suggests that the volume of the crosslinked polymer coil shrinks to 1/30 of the volume of corresponding linear polymer with the same molecular weight. Figure 8 shows the change of g at $[C]_0=10 \text{ g dm}^{-3}$ for evaluating the effect of the number of BAPSX oligomers in a polyimide on the contraction due to intramolecular crosslinking. The value of g decreases with decreasing the number of BAPSX oligomers in a polyimide.

4. Conclusion

The intermolecular crosslinks and the change in polymer coil dimension during the competitive intra- and intermolecular photocrosslinking reactions for the polydimethylsiloxane/benzophenone-containing polyimides were studied in tetrahydrofuran solution. The deviation of ρ from linearity in the initial stage of intermolecular crosslinking becomes progressively greater as the reaction proceeds. This tendency becomes more pronounced as the initial polymer concentration decreases or the number of BAPSX oligomers in a polyimide increases. The second virial coefficient, A_2 , becomes

increasingly smaller as the photocrosslinking reaction proceeds. In particular, the increase of BAPSX oligomers in a polyimide effective for the decrease in A_2 .

The magnitudes of $\langle s^2 \rangle^{1/2}$ and M_w are related to the degree of the competition between intra- and intermolecular crosslinking. The contraction ratio, g , of polymer coils due to intramolecular crosslinking finally becomes 0.1-0.5 at the onset of gelation, showing that the volume of the crosslinked polymer coil shrinks to 1/30-1/3 of the volume of the corresponding linear polymer with the same molecular weight. The magnitude of the contraction of polymer coils increases as the number of BAPSX oligomers in a polyimide decreases.

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