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Complex-Forming Poly(oxyethylene):Poly(acrylic acid) Interpenetrating Polymer Networks.[1] 1. Preparation, Structure, and Viscoelastic Properties

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ABSTRACT: Complex-forming poly(oxyethylene) (POE):poly(acrylic acid) (PAA) interpenetrating polymer networks (IPNs) of equimolar composition were prepared via matrix polymerization of acrylic acid (AA) and a cross-linking agent, ethylene diacrylate (EDA), with pre-cross-linked POE networks of varying effective network chain density ν_E. Especially when ν_E of the POE network was low, the POE:PAA IPNs exhibited a single glass transition due to POE:PAA complex. When ν_E was increased, the loss moduli E'' began to exhibit three loss peaks due to relaxations of the POE-rich phase, the 1:1 POE:PAA complex, and the PAA-rich phase, respectively, from the low-temperature side. When ν_E was further increased, the E'' curves showed only two peaks due to the POE-rich and PAA-rich phases, implying that complex formation is no longer possible between tightly cross-linked POE and PAA networks. Evidence from infrared spectroscopy suggested that POE:PAA complex is formed through hydrogen bonding between the ether oxygens of POE and the carboxylic acid hydrogens of PAA networks.

Introduction

Recently, studies on multicomponent polymers or polymer alloys have been attracting much attention. These materials are noted by their characteristic behavior resulting from the microphase-separated structure. In polymer alloys, phase separation is induced by the immiscibility between their constituent polymers. Generally, most polymer pairs are more or less immiscible and hence incompatible.[2] For improving the compatibility of given polymer pairs, various attempts have been made. One such attempt was the introduction of cross-links within each component to prepare interpenetrating polymer networks (IPNs).[3-5] However, such IPNs still possess microheterogeneity, especially when they are made from immiscible polymer pairs.[3-5] Another possibility for improving the miscibility of polymer blends is to introduce attractive interactions between the components. An example is ionomer blends, in which Coulombic interactions enhance the miscibility of the components.[6,7] Another example is polymer pairs capable of forming an interpolymer complex by a certain specific interaction between the constituent polymers.[8-10]

To obtain miscible and hence highly interpenetrating IPNs, Belonovskaya et al. examined polymerization of mixture of diisocyanates with a variety of polar monomers such as ethylene and propylene sulfides and methacrylates using tertiary amines and benzoyl peroxide as initiators.[11] They discussed the essential features of the IPN formation and proposed some topological models for such IPN systems.[11] On the other hand, Frisch et al. prepared IPNs of prepolymers with ionic groups and were able to increase the extent of interpenetration of the components in the IPNs.[12]

We attempted to introduce a polymer complex into an IPN in order to prepare a highly interpenetrating IPN whose properties may vary reversibly upon changing its chemical environment to induce complex formation and dissociation. In our previous articles, we described preparation and mechanical and thermal properties of a series of IPNs consisting of poly(oxyethylene) (POE) and poly(acrylic acid) (PAA), which form interpolymer complexes through hydrogen bonding.[13,14] Using a specimen of POE:PAA IPN with equimolar composition, we successfully demonstrated its reversible swelling and deswelling[15,16] and also mechanochemical creep and recovery behavior[16,17] upon varying pH and ionic strength of the medium. Furthermore, we prepared a series of equimolar POE:PAA IPNs with varying degrees of cross-linking or densities of effective network chains of the two components by using POE prepolymers with different molecular weights M or by adjusting the content of a cross-linking agent in the PAA networks. Then we examined the effects of the effective network chain density on the structure and viscoelastic properties of the complex-forming POE:PAA IPNs. In this article, we describe the results obtained in this study.

Experimental Section

Materials. Commercially available hydroxyl-terminated poly(oxyethylene) samples (POE; Nakarai Chemicals Co., Ltd.) were used as POE prepolymers. Three samples with catalog

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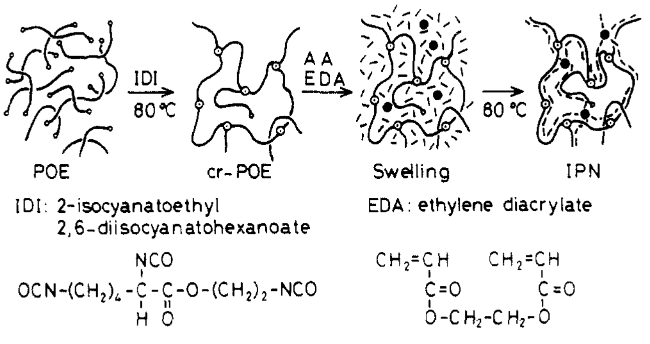

Figure 1. Schematic diagram of the process of POE:PAA IPN preparation.

molecular weights *M* of 300, 600, and 1000 were fractionated with benzene and *n*-hexane.[18] Two other samples with *M* = 2000 and 6000 were purified with hot toluene and *n*-hexane.[14] Acrylic acid (AA) monomer (Wako Pure Chemical Industries, Ltd.) was distilled under a reduced nitrogen atmosphere of 30 torr at 55 °C just before use. The cross-linking agent employed for POE was 2-isocyanatoethyl 2,6-diisocyanatohexanoate (IDI; Toray Industries, Inc.) and that for AA was ethylene diacrylate (EDA; Wako Pure Chemical Industries, Ltd.). The initiator was α,α'-azobis(isobutyronitrile) (AIBN; Nakarai Chemicals Co., Ltd.). IDI, EDA, and AIBN were used as received.

Preparation of IPNs. The procedure for IPN preparation is schematically shown in Figure 1. Each POE prepolymer was mixed with 40 mol % IDI (so that the POE terminal hydroxyl/NCO mole ratio was 1/1) at about 35 °C, just a few degrees above the POE melting temperature. The mixture was kept at 80 °C for 24 h in a sealed polymerization cell. The POE films obtained were kept at room temperature for 10 more days to complete the cross-linking reaction. Then the cross-linked POE films (cr-POE) were swollen to equimolar composition with AA monomer containing 0.5 wt % AIBN and a prescribed amount of EDA. For cr-POE 300 it took 3 h to absorb the AA mixture to the equimolar amount, but for cr-POE 6000 only 3 min. Each swollen film was placed in a sealed polymerization cell and kept for 3 h until the monomer mixture was uniformly distributed in the film. Then the temperature was raised and kept at 80 °C for 48 h to allow AIBN, AA, and EDA to react. The product IPNs were dried under vacuum at room temperature for about a week to remove unreacted monomers. The weight loss during this drying process was negligible, indicating the monomer-to-polymer conversion was nearly 100%.

Two series of IPNs were prepared. In one series—IPN 300 to IPN 6000—POE prepolymers of different molecular weights *M* were used for the first network, but the EDA content *X* in the AA mixture was always 1 mol % for the second network. In the other series—IPN 10E to IPN 0.5E—a POE prepolymer of *M* = 6000 was used for the first network, but *X* was varied from 10 to 0.5 mol % for the second network.

The characteristics of the prepared network samples are summarized in Table I. In the sample codes, cr-POE *M* or IPN *M*, the number *M* indicates the molecular weight of the POE prepolymer, while in the codes, cr-PAA *X*E or IPN *X*E, the symbol *X* indicates the mol % of cross-linker EDA in the AA monomer mixture. If the formation of the PAA network proceeded via matrix polymerization of AA along the POE network chains with occasional cross-linking, the final IPN may possess the structure modeled in Figure 1, which is similar to one of the models proposed by Belonovskya et al.[11]

Characterization of the Samples. Dynamic mechanical measurements were made with a Rheovibron DDV-II (Toyo-Baldwin Co.) at 110 Hz over a temperature range 130–450 K (occasionally to 500 K) with a heating rate of about 1 K min^{-1} under a dry nitrogen stream.

Thermal analyses were made with a differntial scanning calorimeter (Rigaku Denki Model 8055) over a temperature range 180–380 K with a heating rate of 10 K min^{-1}.

Infrared spectra were obtained on a Fourier transform infrared (FTIR) spectrophotometer (JASCO FT/IR-3) by an attenuated total reflection (ATR) method.

Table I
Characteristics of the Network Samples

code	network chain density $10^4\nu$/(mol cm^{-3})		
M[a] or *X*E[b] (M_n)[c]	obsd ν_E[d] eq 1	calcd ν_{II}[e] eq 2 and 3 (or 4)	assumed ν_{EE}[f] eq 1 and 2
cr-POE 300 (401)	14.2	20.2	
cr-POE 600 (666)	8.65	13.6	
cr-POE 1000 (1192)	4.53	8.32	
cr-POE 2000	2.44	5.19	
cr-POE 6000	0.80	1.83	
IPN 300	10.1	9.35	7.37
IPN 600	6.21	6.96	5.36
IPN 1000	4.36	5.05	3.87
IPN 2000	3.31	3.92	3.11
IPN 6000 (1E)		2.70	2.52
IPN 10E	9.12	17.1	16.9
IPN 5E	6.62	9.40	9.22
IPN 2E		4.28	4.16
IPN 0.5E		1.59	1.41
cr-PAA 1E	3.49	(3.19)	

[a] *M* indicates the catalog molecular weight of the POE prepolymer. For all the IPN *M* samples, 1 mol % EDA was used for the PAA network. [b] *X* indicates EDA mol % in AA. For all the IPN *X*E samples, POE of *M* = 6000 was used as the prepolymer. [c] Number-average molecular weight determined by cryoscopy. [d] Estimated ν_E from E' by eq 1. [e] Estimated ν_I or ν_{II} by eq 3 for cr-POE, eq 4 for cr-PAA, and eq 2 for IPNs with ν_I values for cr-POE and cr-PAA. [f] Estimated ν_{EE} by eq 2, replacing ν_I from eq 3 or 4 by ν_E from eq 1.

Results and Discussion

Properties of Cross-Linked POE. Parts a and b of Figure 2 show the temperature dependence of the tensile storage E' and loss E'' moduli for cr-POE, respectively. With increasing temperature, the E' curves for cr-POE 300, 600, and 1000 began to fall rapidly at a certain temperature and reached a rubbery plateau. In the rubbery plateau region, E' was directly proportional to the absolute temperature *T*, each specimen showing the entropic elasticity. The E' curves of cr-POE 2000 and 6000 exhibit a two-stage decrease with temperature: First E' drops rather gradually and then rapidly. Temperatures for the first and second decrease correspond roughly to the glass transition T_g and melting temperatures T_m of the cr-POE, respectively.

This behavior is typical of semicrystalline polymers and implies that substantial crystallization has taken place only in the cr-POE samples composed of the POE prepolymer with large *M* and hence having presumably large molecular weight M_c between the cross-links. Therefore, these samples should also exhibit a rubbery plateau above T_m. However, above T_m, the sample became too soft to confirm this behavior by the Rheovibron.

In Figure 2b, we see that the E'' curves of all the cr-POE samples exhibit a single peak corresponding to the glass transition. However, the peaks of cr-POE 2000 and 6000 have a broad shoulder. The loss maximum temperature T_{max} decreases as M_c increases and finally reaches that of a POE homopolymer with $M = 2.5 \times 10^5$. A similar decrease in T_{max} with increasing M_c or decreasing cross-link density is well-known for cross-linked polymers.[19]

Properties of IPNs. Parts a and b of Figure 3 show plots of E' and E'' vs. temperature *T*, respectively, for five IPN *M* samples with *M* from 300 to 6000. The E' curves, except that for IPN 6000, decrease in two or three steps and reach a plateau at high temperatures. However, unlike the plateaus of cr-POE samples, the E' are not exactly proportional to *T*, presumably because the range of temperatures examined was close to the T_g of PAA. For IPN 6000, E' exhibits a sharp decrease in a single step, and E''

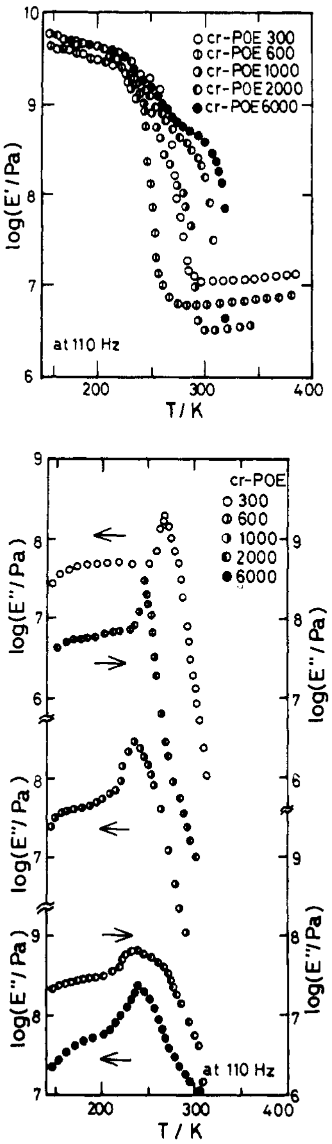

Figure 2. Temperature dependence of (a) tensile storage modulus E' and (b) loss modulus E'' for cr-POE 300, 600, 1000, 2000, and 6000 measured at 110 Hz.

a single sharp loss maximum. On the other hand, IPN 600, 1000, and 2000 exhibited three loss maxima, while IPN 300 exhibited only two maxima.

Parts a and b of Figure 4 show plots of E' and E'' vs. T, respectively, for five IPN XE samples having the same POE 6000 network but a different PAA network with a different amount X of EDA. The E' curves for IPN 10E and 5E decrease with temperature in two steps and then show a rubbery plateau. The E' curves for IPN 2E, 1E (which is the same as IPN 6000), and 0.5E show a rapid single-step decrease.

In Figure 4b, we see that the E'' curves for IPN 10E and 5E show three peaks similar to those of IPN 600, 1000, and 2000. However, the E'' peaks for IPN 10E and 5E, especially the lowest temperature one, are smaller and broader than the corresponding peaks for IPN 600, 1000, and 2000. On the other hand, the E'' curves for IPN 1E and 0.5E show a single sharp peak, and that for IPN 2E shows a single peak with a shoulder at the low-temperature side.

Figure 5 shows typical DSC thermograms of the IPN samples. The arrows indicate the glass transition temperature T_g. IPN 600, 1000, 2000, 10E, 5E, and 2E exhibited three T_g. IPN 6000 (or 1E) and 0.5E exhibited a single glass transition, while IPN 300 showed only two T_g. For IPN 2E, three transitions can be more clearly seen in the DSC thermogram rather than in the E'' curve.

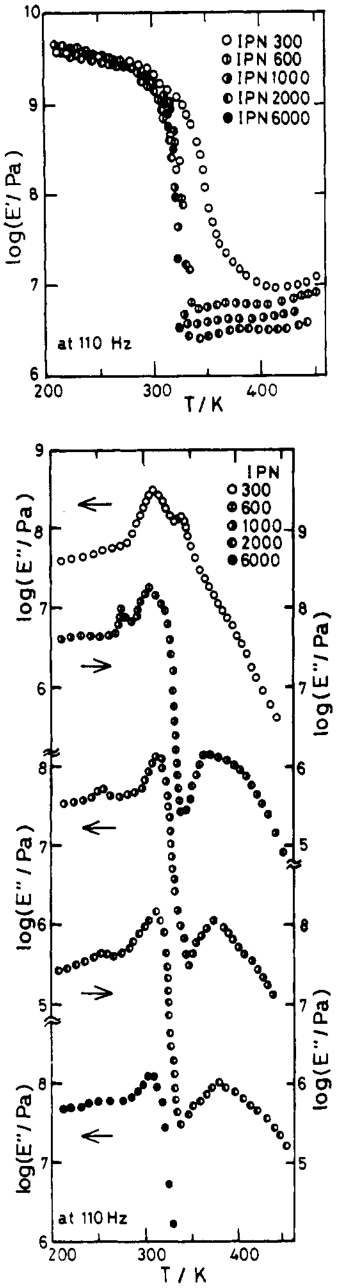

Figure 3. Temperature dependence of (a) tensile storage modulus E' and loss modulus E'' for IPN 300, 600, 1000, 2000, and 6000 measured at 110 Hz.

Judging from T_g and T_{max} data of cr-POE samples and our previous results on 1:1 POE:PAA blend (complex) samples[13,20] and *semi-* and *full*-IPN samples with different POE:PAA compositions,[14,15] we made assignment of the loss peaks as follows. For IPN 600, 1000, and 2000, we ascribed the three loss peaks from the low-temperature side, respectively, to the relaxation of amorphous POE in the POE-rich phase, that of the complex phase, and that of amorphous PAA in the PAA-rich phase. IPN 300 exhibits only two peaks: The high-temperature peak may be ascribed to the PAA-rich phase, but the low-temperature peak may be ascribed to either the POE-rich or the complex phase, which are indistinguishable by T_g or T_{max} data alone. However, the FTIR-ATR result discussed later suggested that in IPN 300 no complex phase appears to exist and that the two loss peaks may be ascribed to the glass transition of the POE-rich and PAA-rich phases. On the other hand, IPN 6000 exhibits a single glass transition, implying it has only the POE:PAA complex phase where

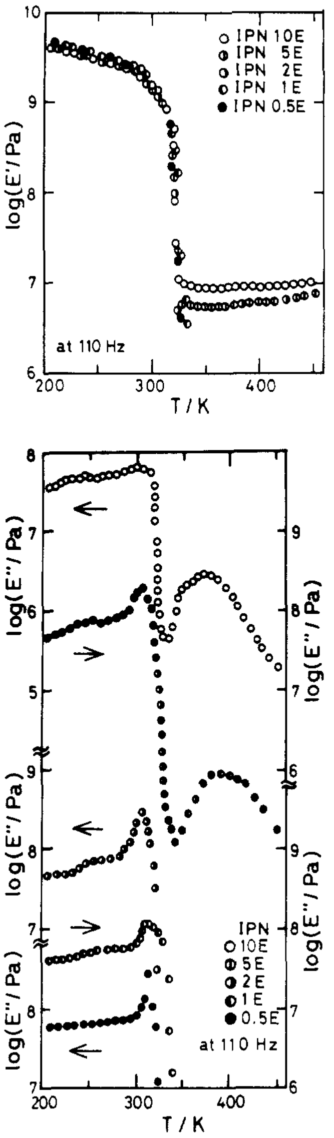

Figure 4. Temperature dependence of (a) tensile storage modulus E' and (b) loss modulus E'' for IPN 10E, 5E, 2E, 6000 (1E), and 0.5E measured at 110 Hz.

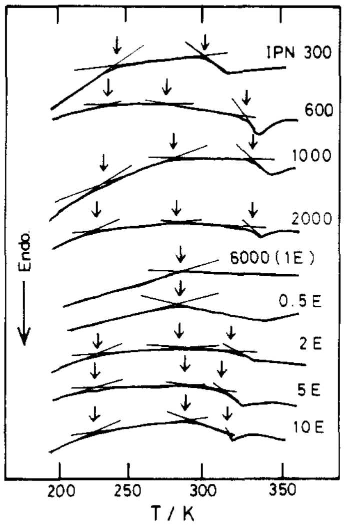

Figure 5. Typical DSC thermograms for POE:PAA IPN samples.

the two network chains are molecularly mixed.

The values of T_{max} are summarized in Figure 6, in which we can see the effects of the effective network chain density on cr-POE and IPNs. Although the T_g data are not shown in Figure 6 to avoid clutter, the behavior of the DSC T_g of the IPN samples corresponds qualitatively to that of dynamic mechanical T_{max} of the same samples. The values of T_g determined by DSC are about 20–40 °C lower than those of the corresponding T_{max} (cf. Figures 5 and 6).

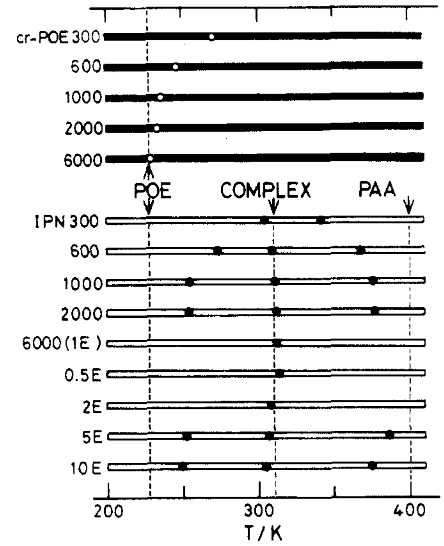

Figure 6. Summary of loss maximum temperatures T_{max} for cr-POE, POE:PAA, and cr-PAA samples.

The T_{max} (or T_g) of the cr-POE decreases with increasing M_c and approaches that of the POE homopolymer with $M = 2 \times 10^5$.

The T_{max} (or T_g) of the POE-rich phase in each IPN appearing at the lowest temperature is always higher than that for the corresponding cr-POE, while that of the PAA-rich phase appearing at the highest temperature is always lower than that of the cr-PAA. They approach those of the respective homopolymers as M_c, especially of the first POE network, is increased. The T_{max} of the POE:PAA complex phase appears between those of the POE-rich and PAA-rich phases, except for IPN 300, which exhibits only two loss peaks, corresponding presumably to those of the POE-rich and PAA-rich phases. However, for IPN 6000 and 0.5E, having a relatively large POE M_c and a low degree of cross-linking in the PAA network, the POE:PAA complex appears to form a dominant phase, and the homopolymer-rich phases disappear. The phase separation appears to be favored in those with larger cross-linking densities. This behavior is entirely opposite to that of common IPNs.[3-5]

In the present IPN, several types of hydrogen bonding are possible: (a) between urethanes inside cr-POE, (b) between carboxyl groups inside PAA, (c) between urethane and carboxyl groups in IPN, (d) between ether and carboxyl groups in IPN, and (e) between hydroxyl and carboxyl groups in IPN. Hydrogen bonds of the a and b type do not favor improvement in the miscibility of the two network components, while those of the c, d, and e type favor improvement of their miscibility. When the cross-linking density in cr-POE is increased or the POE M_c decreases, type a and b hydrogen bonding will increase, but type c, d, and e hydrogen bonding will decrease. As a result, the miscibility of the two components will decrease and phase separation may take place.

It is known that AA monomer polymerizes via matrix polymerization in the presence of POE chains above a certain length, forming an interpolymer complex.[21,22] In the heavily cross-linked POEs, matrix polymerization of AA along the POE network chains may also be hampered, and therefore segregation of the two components may be promoted to some extent. For example, the number of repeating oxyethylene units of the prepolymer for cr-POE 300 and IPN 300 is only 6 or 7. The value 6 or 7 is obviously too small in comparison with the lower limit of the POE molecular weight required for matrix polymerization of AA monomer[22] or complex formation between POE and PAA in aqueous solutions.[23]

On the other hand, in an IPN with low cross-linking density such as IPN 6000 (1E and 0.5E), type c, d, and e hydrogen bonding may be favored over type a and b hydrogen bonding. Especially type d hydrogen bonding between ether and carboxyl groups may be dominant because of the following reasons: The ether/urethane ratio (leading to type c hydrogen bonding) is only 68/1. The ether/hydroxyl end ratio in the POE prepolymer is 68/1, and the hydroxyl ends should be consumed during the end-coupling reaction to from cr-POE so that the amount of residual hydroxyl ends in cr-POE and IPN (leading to type e hydrogen bonding) must be trivial. These factors will allow matrix polymerization and cross-linking of AA on the cr-POE network, leading to the complex-forming IPN through mainly type d hydrogen bonding.

The results of T_{max} of IPN 10E, 5E, 2E, 6000 (1E), and 0.5E also suggest that heavy cross-linking in the second PAA network prevents complex formation, leading to a more or less heterogeneous IPN. However, the effect of cross-linking in the PAA network on viscoelastic properties of IPNs is far smaller than that in the POE network. This result is consistent with the prediction of Sperling[24] on the effects of effective chain densities of the first and second networks on the domain size of IPNs. According to Sperling,[24] one should change the cross-link density of the second network 10 times as much as that of the first network to obtain equal effects on the domain size of the second component.

Estimation of Density of Effective Network Chains in IPNs. According to the theory of rubber elasticity,[25,26] the density ν_E (mol cm^{-3}) of effective network chains may be estimated from E' at the rubbery plateau as

$$E' = 3\nu_E RT \qquad (1)$$

where RT has the usual meaning. Equation 1 may be applied to cr-POE and cr-PAA. Although the IPNs do not exhibit a rubbery plateau, we estimated ν_E for the IPNs, using the values of E' at 440 K, which is well above the T_{max} of the PAA-rich phase.

Using the values of ν_E for the homopolymer networks, we assume a network chain density ν_{EE} of the IPNs as

$$\nu_{EE} = \phi_{POE}\nu_{E(POE)} + (1 - \phi_{POE})\nu_{E(PAA)} \qquad (2)$$

Here, ϕ_{POE} is the volume fraction of the cr-POE network in the IPN. The ν_E and ν_{EE} results are listed in Table I.

On the other hand, if the end-cross-linking reaction of POE proceeded ideally, the kinetic network chain density $\nu_{I(POE)}$ may be defined as

$$\nu_{I(POE)} = \rho(M_n + 2M_{IDI}/3)^{-1} \qquad (3)$$

Here, ρ is the density of the sample; M_n, the number-average molecular weight of the POE prepolymer; and M_{IDI}, the molecular weight of the IDI residue.

Likewise, if the cross-linking of PAA proceeded ideally, the kinetic network chain density $\nu_{I(PAA)}$ may be defined as

$$\nu_{I(PAA)} = \rho[n_A/2(1 - n_A)M_{AA} + M_{EDA}/2]^{-1} \qquad (4)$$

where n_A and M_{AA} are the mole fraction and the molecular weight of AA, respectively, and M_{EDA} is the molecular weight of EDA.

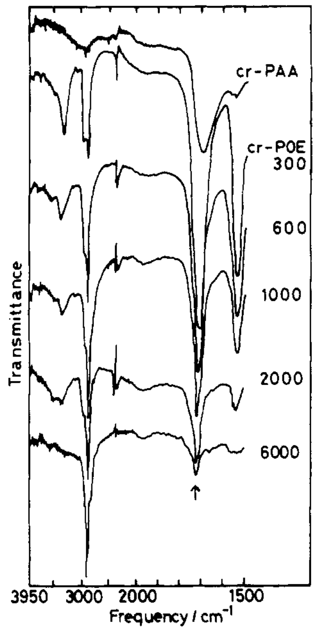

Figure 7. IR spectra of cr-POE and cr-PAA samples.

Then using these ν_I's, we can define a kinetic density of network chains ν_{II} in the IPNs just be replacing ν_E by ν_I in eq 2. The results of ν_I and ν_{II} are also listed in Table I.

For cr-POE, the values of ν_E are always smaller than those of ν_I. That is, the cross-linking efficiency is only about 70 to 45% for POE 300 to POE 6000. This result implies that the urethane end-linking reaction proceeded imperfectly, resulting in formation of some POE idle chains and/or making some IDI acting simply as a chain extender of POE prepolymers. On the contrary, for cr-PAA, ν_E is larger than ν_I. Cross-linking by a copolymerization type reaction always entraps entanglements, enhancing the density of effective network chains.

For the IPNs, we see that the values of ν_E are fairly close to or even exceed those of ν_{II} or ν_{EE}. Since cross-linking efficiency in cr-POE networks is only 75 to 40%, the above result suggests that the effective network chain density is enhanced by interpenetration and also, in some cases, by complex formation between the two constituent networks.

Evidence of Complex Formation between POE and PAA Networks. In a previous article,[14] we described results of solvent extraction experiments on *semi*-IPNs consisting of un-cross-linked POE and cross-linked PAA with varying composition and showed that all excess POE could be quantitatively extracted by 5-h extraction with boiling methanol from the *semi*-IPNs of unequimolar POE:PAA composition. This results implies that POE was presumably forming a 1:1 complex with cr-PAA, and thus, the complex-forming portion of the un-cross-linked POE was not extractable. However, since this evidence was rather indirect, we sought by employing IR spectroscopy other evidence of complex formation in the equimolar *full*-IPNs, in which both components were cross-linked and hence unextractable.

Figure 7 shows IR spectra of cr-POE and cr-PAA samples. For the former, typical absorption peaks of secondary amide, namely N–H stretching, C=O stretching, and N–H deformation, were observed at about 3300, 1700, and 1550 cm^{-1}, respectively. These absorptions reflect the urethane structure resulted from the end-linking reaction of POE and IDI. Several absorption peaks due to C–H stretching of methylene units of POE were also observed. Their intensity relative to that of the secondary amide absorption

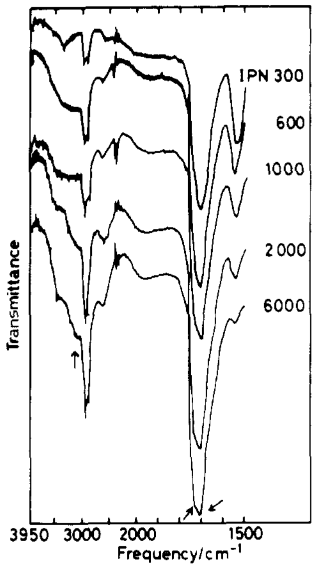

Figure 8. IR spectra of POE:PAA IPN 300, 600, 1000, 2000, and 6000 samples.

increases as M of the POE prepolymer is increased.

On the other hand, the IR spectra of cr-PAA hardly varied from that of PAA without cross-linking.[27] Broad absorption peaks due to O–H and C=O stretching were observed at 3000 and 1700 cm^{-1}, respectively. This result suggests that carboxylic acid groups of cr-PAA (and un-cross-linked PAA as well) may have a dimer structure resulting from hydrogen bondings between the carboxylic groups.[28-31]

Figure 8 shows IR spectra of IPN 300, 600, 1000, 2000, and 6000. The IR spectrum of IPN 300 exactly matches the sum of those of cr-POE 300 and cr-PAA 1E. This results confirms that there is no complex formation or interactions of any type between POE and PAA in IPN 300. On the other hand, the IR spectra of other IPNs exhibit a new absorption peak at 3100 cm^{-1} as compared with those of the corresponding cr-POE and cr-PAA. This absorption at 3100 cm^{-1} appears to be characteristic of the stretching mode of carboxylic O–H groups hydrogen bonded with the ether oxygens in the POE network, because the hydrogen-bonded O–H stretching absorption of carboxylic acids was usually observed at the same 3100 cm^{-1} in ether or proton-acceptor type solvents such as dioxane.[28]

The frequency of the C=O stretching absorption of carboxylic acids is also known to be affected by hydrogen bonding. The C=O stretching absorption of carboxylic acids was observed at 1750 cm^{-1} for the monomeric state without hydrogen bonds and shifted to 1700 cm^{-1} for the dimeric structure with hydrogen bonds.[28-31] On the other hand, the wavenumber of the C=O stretching absorption of carboxylic acids in ether or dioxane usually appears at 1730 cm^{-1}, about 20 cm^{-1} smaller than that without hydrogen bonds in dilute carbon tetrachloride solutions.[32] Thus, the relative intensity of the absorption at 1730 and 1700 cm^{-1} may be taken as the ratio of hydrogen bonds of the carboxylic acid:ether complex to that of the dimeric carboxylic acid structure.

In Figure 8, we see that the intensity of the C=O stretching absorption at 1730 cm^{-1} increases with increasing M of the POE prepolymer. This result suggests that the POE:PAA complex is absent in IPN 300, and in other IPNs with increasing M_c, the extent of POE:PAA complex through hydrogen bonds increases. This behavior resembles that of POE:poly(methacrylic acid) blends with varying POE molecular weight.[33] This observation by IR spectroscopy is consistent with those of dynamic mechanical and thermal analyses.

Conclusion

Lightly cross-linked IPNs of POE and PAA of equimolar composition prepared via matrix polymerization of the latter on the former gave a homogeneous multicomponent system, stabilized by complex formation mainly through hydrogen bonding between the ether oxygens of POE and the carboxylic acid hydrogens of PAA. However, the POE:PAA complex phase disappeared and phase separation took place between the component networks as the cross-link density, especially in the first POE network, was increased.

Acknowledgment. We thank Dr. D. Klempner for the suggestion on the types of possible hydrogen bonding in the present IPN system and their implication on the IPN formation with a high degree of interpenetration. This work was supported in part by the Ministry of Education, Science and Culture (Mombusho) through Grant 543026 during 1980–1982, which is gratefully acknowledged.

Registry No. (POE)·(IDI) (copolymer), 97042-87-0; (EDA)·(AA) (copolymer), 52641-03-9; (POE)·(IDI) (copolymer)–(EDA)·(AA) (copolymer), 97042-88-1.

References and Notes

(1) To distinguish various topologically different species of polymer alloys (multicomponent polymers) made from the same constituent polymers, say, poly(A) and poly(B), we employ the following convention: Block and graft copolymers are designated as poly(A)–poly(B); polymer blends and interpenetrating polymer networks (IPN) as poly(A)/poly(B), in which the presence of covalent bonds between the two components is unimportant; and polymer complexes of complex-forming systems as poly(A):poly(B), in which specific secondary interactions such as hydrogen bonds prevail. Along the same line, random copolymers may be designated as copoly(AB).
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Chelating Copolymers Containing Photosensitive Functionalities. 3. Photochromism of Cross-Linked Polymers

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ABSTRACT: A series of cross-linking agents of azobenzene with amide and sulfonamide spacer groups were prepared. Several homo- and copolymers were prepared with the azo cross-links by radical polymerization using AIBN initiator. The polymers undergo typical photochemical cis–trans isomerism to varying degrees. The thermal relaxation data indicate the importance of the structural and steric environment surrounding the cross-links. For example, a bulky phenyl substituent next to azobenzene seems to retard the photoisomerization. The nature of the polymeric matrix and the molecular weight did not affect the degree of isomerization, and the cis–trans cycle could be carried out without any fading. There was also no photoviscosity effect.

Introduction

The cis–trans isomerism of azobenzene moieties has recently been utilized as a photosensitive "switch" to regulate physical and chemical phenomena.[1-3] From the literature, it is obvious that the nature and the morphology of the polymer have an essential influence on the photo- and thermochromism of a chromophore in a given polymer matrix. The photochemical isomerism and the thermal isomerism of aromatic azo chromophores dissolved in a polymer matrix,[4,5] those wth a pendant group, or those which were part of the polymer backbone[6-11] have been investigated extensively. It was concluded that photochromic processes in bulk polymers are linked to particular motions of chain segments[12,13] and that the relaxation behavior of the photochrome depends on the free volume as described by a form of the WLF equation.[13]

The remaining question is how the photochromism of azo groups lodged in the cross-links would be influenced by the nature of the polymer matrix and by the presence or absence of spacer groups separating it from the main chains. Eisenbach investigated the photomechanical changes (i.e., a reversible contraction and expansion of such an oriented rubbery film upon irradiation based on change of dimensions of the cis and trans form of the azo chromopore) due to the isomerization of azo cross-links in poly(ethyl acrylate) networks and concluded that the same parameters of chain segmental mobility and of free volume as found for pendant groups, e.g., linear polyacrylates of polymethacrylates, are valid.[14]

The combination of a chelating group and a readily isomerizable group in a macromolecule whose physical and mechanical properties can be controlled by an external source presents the possibility of a structurally modifiable photosensitive ion switch. We have reported earlier the incorporation of azo aromatic groups in bipyridine- and pyridine-based macromoleular ligands and studied their complexing behavior under irradiation.[15-17] A detailed investigation of structure and morphology of a family of polymers on the behavior of photochromic cross-links and the effect of spacer arms separating it from the backbone is necessary for the construction of macromolecular ligands with photochromic cross-links. The photochemical and thermal cis–trans isomerizations of the azo aromatic cross-links in different structural and steric environments are described in this paper.

Experimental Section

4,4′-Divinylazobenzene was prepared by the same sequence of reactions that we reported earlier for the synthesis of 4,4′-divinylbenzophenone[18] (Figure 1).

Synthesis of 4,4′-Dimethylazobenzene.[19] To a solution of 109.7 g (0.8 mol) of *p*-nitrotoluene dissolved in 1 L of MeOH contained in a three-necked round-bottom flask equipped with a condenser and mechanical stirrer was added a solution of 130.0 g (3.24 mol) of NaOH dissolved in 300 mL of H_2O. The mixture was stirred and 106 g (1.64 mol) of Zn dust was added. The reaction mixture was refluxed for 11 h and filtered while still hot. Evaporation of the filtrate gave an orange product. Part of the product that remained in the filter was extracted with acetone, which on evaporation gave more of the product. The combined products were then stirred in 2% HCl, warmed, and filtered. The product was washed several times with hot water and then recrystallized from EtOH. The orange crystals of Ia were dried under vacuum: yield 50 g; mp 134 °C; NMR δ 2.32 (s, 6 H), 7.1–7.9 (2 d, 8 H).

4,4′-Bis(bromomethyl)azobenzene. A mixture of 19.5 g (92.8 mmol) of 4,4′-dimethylazobenzene, 36 g (202 mmol) of *N*-bromosuccinimide (NBS), and 0.6 g of benzoyl peroxide in 250 mL of CCl_4 was heated under reflux for 3 h, after which the yellow color of the NBS had disappeared. The mixture was cooled in ice water and filtered with suction, the filtrate was washed thoroughly with water and dried over $MgSO_4$, and the solvent was evaporated. The residue was recrystallized from CCl_4, yielding

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