(38.08 g, 235 mmol) in THF (100 mL), was added dropwise to a stirred solution of $(NPCl_2)_n$ (4 g, 3.45×10^{-2} mol) in THF (350 mL) at room temperature. After the addition was complete, the reaction mixture was heated to 50 °C for 16 h and then cooled to room temperature. The polymer was recovered by precipitation into water, and this process was repeated twice, followed by precipitation from THF into methanol twice. The polymer was further purified by Soxhlet extraction with ethanol for 96 h and was dried under vacuum. Characterization data are listed in Table VI.

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Registry No. **6**, 940-71-6; **7**, 811-41-6; **8**, 111409-20-2; **9**, 111435-05-3; **10**, 42861-68-7; **11**, 111409-21-3; **12**, 5032-39-3; **13**, 101671-97-0; **14**, 111409-22-4; **15**, 111409-23-5; **16**, 101671-98-1; **17**, 111435-06-4; **18**, 111409-24-6; **19**, 85251-38-3; **20**, 86549-55-5; **21**, 111409-25-7; **22**, 111409-26-8; **23**, 111409-27-9; **24**, 111409-28-0; **25**, 111409-29-1; $NaOCH_2C_6H_5$, 20194-18-7; 4-$NaOCH_2C_6H_4C_6H_5$, 111409-30-4; 4-$NaOCH_2C_6H_4Br$, 111409-31-5; 4-$NaO(CH_2)_2C_6H_5$, 22096-25-9; 4-$NaO(CH_2)_3C_6H_5$, 111409-32-6; 4-$NaOC_6H_4CHO$, 22666-84-8; 4-$H_2NC_6H_4OCH_3$, 104-94-9; 4-$H_2NC_6H_4OH$, 123-30-8; 4-$ClCOC_6H_4OCH_3$, 100-07-2; 4-$ClCOC_6H_4CN$, 6068-72-0; 4-$NaOC_6H_4NO_2$, 824-78-2; 4-$OHCC_6H_4OCH_3$, 123-11-5; 4-HOC_6H_4CHO, 123-08-0; 4-$OHCC_6H_4CN$, 105-07-7.

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Miscibility of Poly(2-oxazolines) with Commodity Polymers

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ABSTRACT: Poly(*N*-acylethylenimines) (PMeOZO, PEtOZO, and PPrOZO) have been examined for miscibility with commodity polymers of poly(vinyl chloride) (PVC), polystyrene (PSt), polypropylene (PP), and poly(vinylidene fluoride) (PVF_2). The miscibility of polymer blends has been investigated by three methods: dynamic viscoelastic behaviors by rheovibron for all commodity polymer blends, differential scanning calorimetry, and wide-angle X-ray scattering, the latter two being for PMeOZO–PVF_2 blends. PMeOZO–PVC and PMeOZO–PVF_2 blends are miscible at the range of the PMeOZO fraction lower than 50 wt %. With the PMeOZO–PVF_2 blend system, miscibility is discussed for the amorphous and crystalline parts of PVF_2. PPrOZO is miscible with PSt when the PPrOZO is up to at least 25 wt %. Both PMeOZO–PP and PEtOZO–PP blends are not miscible.

Introduction

Polymer blends have recently received much attention with respect to development of new composite materials. In blending systems, miscibility (or compatibility) of polymers is very important since it affects the properties of the resulting polymer blend.[1-3] Accordingly, the usefulness of a polymer is increased when the polymer is made miscible (compatible) with other polymers. A recent report represents the studies of such direction; when *N*,*N*-dimethylacrylamide monomer unit is incorporated into

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polyethylene, the polymer becomes miscible with poly(vinyl chloride) (PVC).[4] Miscibility of polymer blends has been studied by various techniques such as thermal,[5-9] dynamic mechanical,[4,7] and dilatometric[6] analysis.

Poly(N-acylethylenimines) (PROZO) derived from 2-oxazolines are slightly "basic" polymers due to the amide structure. Therefore, PROZO is expected to be miscible with a slightly "acidic" polymer such as PVC.[4] Miscibility of poly(N-propionylethylenimine) with styrene-acrylonitrile copolymers has been examined by using differential scanning calorimetry; the former polymer was found to be miscible with the copolymers having compositions in the range of about 20-40 wt % of acrylonitrile.[9] We have already reported preliminary results on miscibility studies of PROZO with some commodity polymers mainly by measuring dynamic viscoelastic behaviors of the film of polymer blends with rheovibron.[10,11] The present paper describes these results, in which three kinds of PROZO (R = CH_3, C_2H_5, and n-C_3H_7) and four commodity polymers of PVC, polystyrene (PSt), polypropylene (PP), and poly(vinylidene fluoride) (PVF_2) are employed. The present results also provide fundamental data in establishing the role of "compatibilizer" of poly(N-acylethylenimine) chain between cellulose diacetate-*graft*-poly(N-acylethylenimine) and PVC.[12] and PVC.[12]

Experimental Section

Materials. Poly(N-acetylethylenimine) (PMeOZO) and poly(N-butyrylethylenimine) (PPrOZO) were obtained by ring-opening polymerization of 2-methyl-2-oxazoline (MeOZO) and 2-n-propionyl-2-oxazoline(PrOZO) initiated by methyl p-toluenesulfonate in acetonitrile. $\overline{DP}$ values of these polymers determined by vapor pressure osmometry in $CHCl_3$ were 54 and 45, respectively. Poly(N-propionylethylenimine) (PEtOZO) ($\overline{DP}$ = 500) was supplied by Dow Chemical Co., Midland, MI. PVC ($\overline{DP}$ = 450) and PP ($\overline{DP}$ = ~8300) were obtained from Sumitomo Chemical Co., Osaka. PVF_2 ($\overline{DP}$ = 700-860) was given by Kureha Chemical Co., Tokyo. A commercial sample of PSt ($\overline{DP}$ = ~1500) was employed. Solvents, CH_2Cl_2, $CHCl_3$, and DMA, were purified by distillation.

Preparation of Samples for Torsional Braid Analysis. In a 5 wt % $CHCl_3$ solution of PMeOZO (or PEtOZO, PPrOZO) a glass-fiber braid was dipped overnight. Then, $CHCl_3$ in the braid was evaporated at room temperature in air and, then, in vacuo for 10 h. The PMeOZO-coated braid contained about 6.4% of PMeOZO by weight for the total braid sample.

Preparation of Blend Sample Films for Rheovibron Measurements. Sample films of the PMeOZO-PVC blend were prepared by casting from a CH_2Cl_2 solution. A mixture (0.3 g) of PMeOZO and PVC with a desired ratio was stirred in 6 mL of CH_2Cl_2 for 24 h at room temperature to give a homogeneous solution. The solution was transferred into a Teflon box and the solvent was allowed to evaporate under atmospheric pressure at room temperature. The resulting film was further dried in vacuo at 5 h and cut to a sample film size of 30 mm × 3 mm with 0.15-mm thickness for rheovibron measurements.

Blend sample films of PROZO-PSt were prepared in a similar way as the above except by that $CHCl_3$ was used as casting solvent.

Blend films of PMeOZO-PP and PEtOZO-PP were prepared by using a kneader (Ueshima Seisakusho Co.) at melt. A mixture of PMeOZO (or PEtOZO) and PP pellets was well mixed in the kneader at 200 °C and its film was formed by molding. The film was annealed at 120 °C for 2 h and then cooled down to room temperature gradually.

The PMeOZO-PVF_2 blend films were also prepared as in the case of the PMeOZO-PVC blend except that DMA was used as casting solvent. To obtain a homogeneous solution, the mixture was subjected to ultrasonication. For casting, DMA was evaporated in vacuo at room temperature for 2 h and then at 50 °C for 4 h. Complete evaporation of DMA was confirmed by IR measurement of the resulted film. For annealing, the sample film was kept at 110 °C for 1 h and cooled gradually to room temperature.

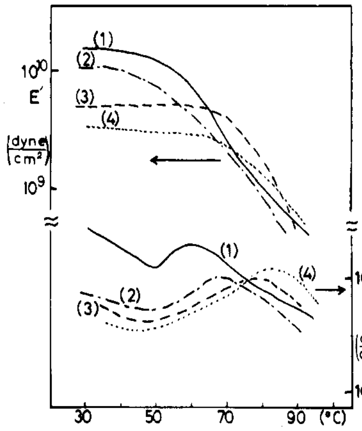
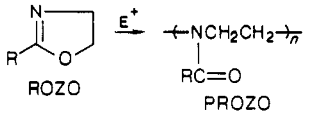


Figure 1. Dynamic modulus (E′) and loss modulus (E″) versus temperature for (1) PVC, (2) PMeOZO-PVC (1:9) blend, (3) PMeOZO-PVC (1:3) blend, and (4) PMeOZO-PVC (1:1) blend.

Measurements. Dynamic mechanical properties (G) of homopolymers, PMeOZO, PEtOZO, and PPrOZO, were examined by a free-oscillation torsion pendulum of RD-100 type (Rhesca Co. Ltd. Japan). Dynamic mechanical properties, E′ and E″, of blend sample films were measured at 110 Hz by a rheovibron viscoelastometer of DDV-II-C type (Toyo Baldwin Co. Ltd.). DSC measurements were carried out on a DS-2C-TADS type differential scanning claorimeter (Perkin-Elmer Co.). The wide-angle X-ray measurements of PMeOZO-PVF_2 blends were carried out on a D-60 type X-ray diffractometer (Rigaku Denki Co.) with nickel-filter Cu Kα radiation.

Results and Discussion

Poly(N-acylethylenimines) (PROZO) are prepared by the cationic ring-opening polymerization of 2-alkyl-2-oxazolines (ROZO). Three kinds of polymers, PMeOZO, PEtOZO, and PPrOZO, are employed. Degree of polymerization (DP) data are given below. The glass transition temperature (T_g) was determined by torsional braid analysis (TBA). The maximum value of mechanical loss (tan δ) corresponds to T_g, which is 85 °C for PMeOZO. These data for other two polymers are also given. In a literature,[13] the T_g values of these polymers have been reported as ~80, ~70, and ~30 °C, respectively.



PMeOZO(R = Me): $\overline{DP}$ = 54; T_g = 85 °C
PEtOZO(R = Et): $\overline{DP}$ = 500; T_g = 70 °C
PPrOZO(R = n-Pr): $\overline{DP}$ = 45; T_g = 28 °C

PMeOZO-PVC Blends. Film specimens of PVC and of three blends were prepared by casting from CH_2Cl_2 solution. Their dynamic mechanical properties were measured at 110 Hz by using a rheovibron viscoelastometer.[14] Figure 1 shows dynamic modulus (storage modulus) E′ and loss modulus E″ as a function of temperature. The E″-temperature relationship gives a better indication of miscibility since the maximum of E″ corresponds to T_g. The E″ maximum of PVC alone is 58 °C (curve 1). In blending systems, this value shifts to 67 °C (curve 2), 78 °C (curve 3), and 83 °C (curve 4) with increasing the content of PMeOZO to 10%, 25%, and 50%, respectively, approaching that of 85 °C for PMeOZO alone. Each curve (2)-(4) shows only single E″ maximum in the intermediate region between that of PVC and PMeOZO. These results clearly indicate that PMeOZO and PVC are completely miscible with each other to form a single phase.

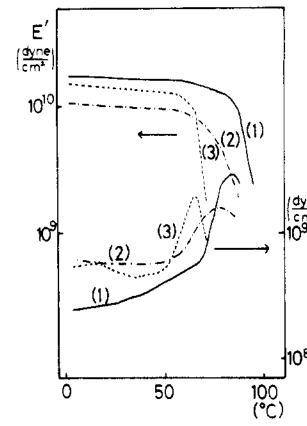


Figure 2. Dynamic modulus (E') and loss modulus (E'') versus temperature for (1) PSt, (2) PPrOZO–PSt (1:9) blend, and (3) PPrOZO–PSt (1:3) blend.

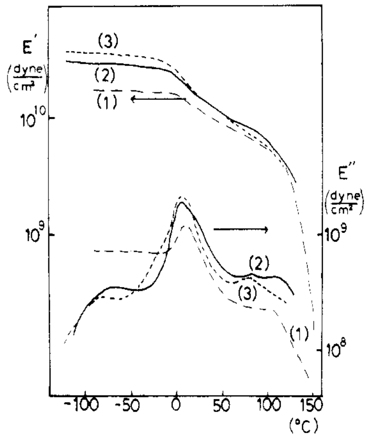
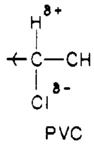


Figure 3. Dynamic modulus (E') and loss modulus (E'') versus temperature for (1) PP, (2) PMeOZO–PP (1:9) blend, and (3) PEtOZO–PP (1:9) blend.

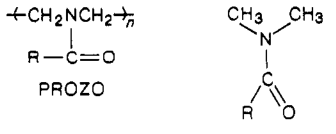
This good miscibility of PMeOZO and PVC is probably due to an effective interaction between a weakly acidic hydrogen of PVC and a slightly basic amide group of PMeOZO as discussed above.



$-\!\!\left(\overset{H^{\delta+}}{\underset{Cl^{\delta-}}{C}}-CH_2\right)\!\!-_n$

PVC

PPrOZO–PSt Blends. PROZO can be taken as a polymeric derivative of *N,N*-dimethylacetamide (DMA) or *N,N*-dimethylformamide (DMF). PSt has no strong electron-withdrawing group. But, it is soluble in a dipolar aprotic solvent such as DMA or DMF, and hence, miscibility between PSt and PROZO is expected. The E''_{max} of PSt (molecular weight = 1.6×10^5) is 78 °C (Figure 2, curve 1). For the analysis by rheovibron, the T_g's of two polymers should be apart to some extent. Therefore, PPrOZO was chosen, whose T_g is 28 °C. In the blending system, the content of PPrOZO was increased from 10% up to 25%. Then, only single E''_{max} was observed and shifted to the lower value as shown in curves 2 and 3 (Figure 2). The 1:1 blend, however, behaved differently. During the casting of the film, macrophase separation was clearly observed. Thus, complete miscibility is achieved within a limited range of blending ratio, i.e., the content of PPrOZO lower than ~50%.



$-\!\!\left(CH_2\underset{R-C=O}{N}CH_2\right)\!\!-_n$ PROZO $\qquad (CH_3)_2N-C(=O)R$

DMA or DMF

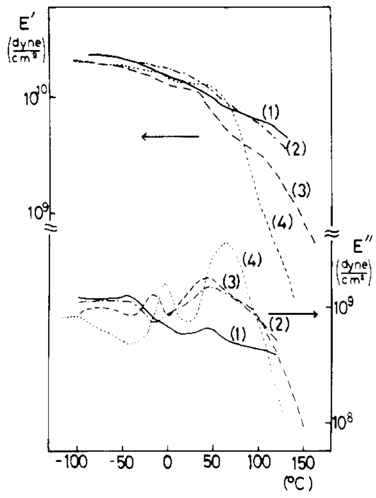


Figure 4. Dynamic modulus (E') and loss modulus (E'') versus temperature for 1) PVF_2, (2) PMeOZO–PVF_2 (1:9) blend, (3) PMeOZO–PVF_2 (1:3) blend, and (4) PMeOZO–PVF_2 (1:1) blend.

PMeOZO–PP and PEtOZO–PP Blends. The molecular weight of sample PP is 350 000. The E''_{max} of this PP is 10 °C as shown by curve 1 (Figure 3). Film specimens of blend systems were prepared as follows. A mixture of PMeOZO (or PEtOZO) and PP (1:9) was well blended in a kneader at 200 °C, a film of the blend was made on a molding press, and then, the film was annealed at 120 °C for 2 h. In both blending systems, two E'' maximums were observed: at 10 °C (strong) and at around 85 °C (weak) in the PMeOZO–PP blend (curve 2) and at 10 °C (strong) and at around 75 °C (weak) in the PEtOZO–PP blend (curve 3, Figure 3). These two E''_{max} values are due to the individual homopolymers in both cases and the blends do not form a single phase. It is concluded, therefore, that PMeOZO–PP and PEtOZO–PP are not miscible systems.

PMeOZO–PVF_2 Blends. Film specimens for rheovibron measurements have been prepared by casting method; from a DMA solution of PVF_2 alone or of a PMeOZO–PVF_2 mixture, DMA was evaporated in vacuo at 50 °C. Dynamic mechanical properties of PVF_2 have been studied extensively by different researchers.[15-17] Three significant relaxations have been observed, which are designated α, β, and γ dispersions. As seen in Figure 4, PVF_2 itself (without annealing) shows E'' maximums at 40 °C due to α dispersion and at −50 °C due to β dispersion. The γ process is generally weak and not observed in Figure 4. The α and β processes are attributed respectively to the molecular motions associated with crystalline regions and their defects and to the motion of the main chain in amorphous regions (and thus may be regarded as responsible for T_g).[17] In blending systems of PMeOZO–PVF_2, β dispersion is affected very much. With increasing the content of PMeOZO to 10%, 25%, and 50%, the E''_{max} shifted to −47, −20, and 0 °C, respectively (curves 2, 3, and 4). The E''_{max} of α dispersion also shifted to higher temperatures, although the extent of the shift is small probably because the crystalline regions of PVF_2 are hardly affected by blending with PMeOZO. These results indicate that PMeOZO is miscible with PVF_2 up to at least 50% by weight.

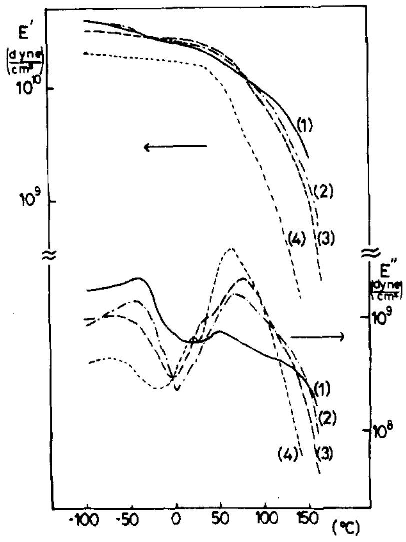


Figure 5. Dynamic modulus (E') and loss modulus (E'') versus temperature for (1) PVF_2, (2) PMeOZO-PVF_2 (1:9) blend, (3) PMeOZO-PVF_2 (1:3) blend, and (4) PMeOZO-PVF_2 (1:1) blend. All sample films were annealed at 110 °C for 1 h.

Table I
Results of DSC Analysis for PMeOZO-PVF_2 Blend Samples Annealed at 110 °C for 1 h

PVF_2/ (PMeOZO + PVF_2), %	T_g, °C	T_m, °C	H_m, cal/g
100		174.1	16.6
90	55.5	174.6	15.2
80	63.6	172.2	14.3
75	66.1	171.3	12.6
60		169.9	10.9
50	73.3	165.8	8.0

Film samples annealed at 110 °C for 1 h behaved differently (Figure 5). An annealed PVF_2 film showed E'' maximums of α dispersion at 48 °C and that of β dispersion at −40 °C (curve 1). It is to be noted in blending systems that α dispersion became stronger due to higher crystallinity with annealing (curves 2, 3, and 4), whereas β dispersion disappeared. The change of E'' maxima with blends having 10% and 25% of PMeOZO was similar to those of unannealed samples, i.e., the E'' values of these two blends of annealed samples were 67 and 78 °C, respectively. But the 1:1 blend showed a rather lower E''_{max} of 65 °C (curve 4). These phenomena of α dispersion may be explained as follows. With the PMeOZO content lower than 25%, PMeOZO and crystalline regions of PVF_2 form a well-dispersed system, and hence, the E''_{max} appears at an intermediate range between those of PVF_2 (48 °C) and PMeOZO (85 °C). With the 50%-50% blend, on the other hand, both polymers are not completely miscible and PVF_2 forms its own crystalline regions by annealing. Thus, the E''_{max} appears at a lower temperature than that of completely miscible cases. This view is also confirmed by wide-angle X-ray scattering (vide infra).

Differential scanning calorimetry (DSC) is also an effective method to examine the miscibility of polymer blends, e.g., a PVF_2-poly(ethyl methacrylate) system.[18] Here the PMeOZO-PVF_2 blend was investigated by DSC in the temperature range 30-220 °C. Film specimens of the blend were prepared similarly to those of rheovibron measurements. From the DSC diagram, T_g, melting temperature (T_m), and enthalpy of melting (ΔH_m) of a series of blends have been obtained (Table I). The values of T_g and T_m changed monotonously, going up (T_g) and down (T_m) with increasing fraction of PMeOZO in PMeOZO-PVF_2 blends.[18] It is very clear from these results that both polymers are miscible for the five compositions examined.

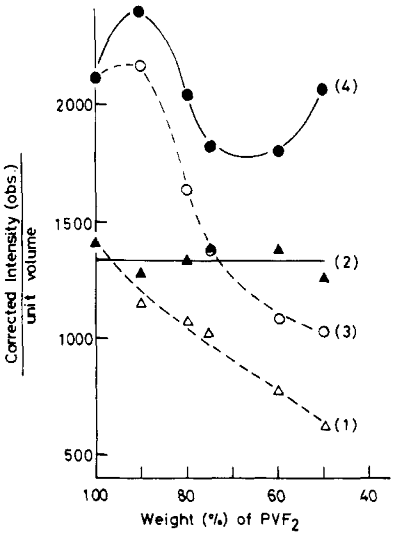


Figure 6. Corrected intensities observed in the wide-angle X-ray scattering of PVF_2-PMeOZO blends as a function of weight percent of PVF_2: (1) observed intensity of blend samples without annealing; (2) calculated intensity for the net PVF_2 in blends without annealing; (3) observed intensity of blends annealed at 110 °C for 1 h; (4) calculated intensity for the net PVF_2 in annealed blends.

Since the dynamic mechanical behavior of blending systems examined by rheovibron was complicated due to the crystalline nature of PVF_2, the miscibility of PMeOZO-PVF_2 blends has been investigated further by wide-angle X-ray scattering. Film specimens were prepared in a similar manner as those for rheovibron measurements. The wide-angle X-ray scattering diagram of PVF_2 shows two peaks; a larger one at $2\theta = 35.3°$ due to crystal form I (001) and a smaller one at $2\theta = 39.0°$ due to crystal form II (002).[19,20]

Figure 6 shows the X-ray scattering intensity of PMeOZO-PVF_2 blends as a function of weight percent of PVF_2, in which the intensity is the sum of two peak intensities obtained by taking the structural factor into account.[18] For blend samples without annealing the observed intensity decreased simply with decreasing the PVF_2 fraction (curve 1). But the intensity per net weight of PVF_2 in the blend is not changed (curve 2). This phenomenon suggests that the crystalline part of PVF_2 is not affected at all, and hence, PMeOZO forms a single phase with the amorphous part of PVF_2. These observations are very compatible with those of rheovibron analysis.

Annealed blend samples, on the other hand, behaved differently (curves 3 and 4). All samples had increased intensities, i.e., the crystallinity, in comparison with samples without annealing. Note that the blend sample having 90% PVF_2 showed somewhat stronger intensity than the sample of neat PVF_2. This is due to that after annealing the crystalline part of PVF_2 grows because the presence of PMeOZO (10%) prevents the heat dispersion and the rapid cooling of the blend. With increasing PMeOZO fraction, 20%, 25%, and 40%, the intensity decreased. This is because PMeOZO is miscible also with a part of the crystalline regions of PVF_2 and the crystalline part of PVF_2 decreased. The 1:1 blend, however, increased in intensity, indicating that the blend is partly immiscible. These observations again support the results of rheovibron analysis.

The results by wide-angle X-ray scattering indicate that without annealing PMeOZO is miscible only with amorphous parts of PVF_2 whereas with annealing PMeOZO becomes miscible with not only the amorphous part but also some of the crystalline part (probably surrounding regions of the crystalline part) of PVF_2. And the fraction of PMeOZO is limited constructing a miscible phase in the PMeOZO–PVF_2 blend (<50%).

Conclusion. PMeOZO–PVC and PMeOZO–PVF_2 blends are miscible in the blend fraction range of PMeOZO lower than 50 wt %. PPrOZO is miscible with PSt in the range of the PPrOZO fraction lower than 25 wt %. Both PMeOZO–PP and PEtOZO–PP blends are not miscible. These results provide fundamental, important data when new polymer materials are desired from blends of these polymers and/or copolymers.

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Registry No. PVC, 9002-86-2; PSt, 9003-53-6; PP, 9003-07-0; PVF_2, 24937-79-9; PMeOZO (homopolymer), 26375-28-0; PMeOZO (SRU), 25805-17-8; PEtOZO (homopolymer), 25822-74-6; PEtOZO (SRU), 38796-76-8; PPrOZO (homopolymer), 69488-61-5; PPrOZO (SRU), 25821-74-3.

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Molecular Motions in Model Network Polymers

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ABSTRACT: Molecular motions in network polymers of monodisperse PPO, α,ω-dihydroxypoly(propylene oxide), cross-linked with TIPTP, tris(4-isocyanatophenyl) thiophosphate, were compared with those of linear polymers of the same molecular weight PPO chains extended with diisocyanates. The linear polyurethanes have a single exponential decay for $T_{1\rho}$(C) with well-defined $T_{1\rho}$(C) minima that occur at lower temperatures for longer PPO segments. Samples of 1000 MW PPO chains extended with phenylene-1,4-diisocyanate show the same $T_{1\rho}$(C) values by cross polarization or direct polarization while these values are different for toluene-2,4-diisocyanate linked polymers, indicating the presence of regions of dissimilar rigidity. The decay of backbone carbon magnetization is biphasic for networks with PPO MW 400–2000. The fast components have values very close to the corresponding $T_{1\rho}$(C) value for the aromatic carbons. The former is probably the relaxation of those backbone atoms in proximity with and closely coupled to the phenyl group of TIPIP while the slow component is associated with the remote backbone carbons. The networks formed from MW 3000 PPO have $T_{1\rho}$(C) behavior resembling that for the linear polyurethanes according to both cross and direct polarization. CP-MAS-^{13}C NMR thus yields a biphasic decay for networks with short interconnecting chains, but when the length of chains approaches 3000, the relaxation becomes simple exponential and closely resembles that of linear chain systems.

Cross-linked polymeric systems span a wide range of properties and applications from swollen gels of hydroxyethyl methacrylates to rubbers, engineering resins, and composite matrix materials. Physicochemical measurements on these systems are naturally limited to those which do not require their dissolution. Most of the techniques measure the macroscopic properties. Any new method that can reveal details of the molecular motion and indeed any discrimination of regions within a network would contribute toward further advances in the basic understanding and designing of new network systems.

There is extensive literature on nuclear magnetic relaxation in polymeric networks and rubbery materials. Early work relied upon the decrease with temperature of the second moment of the featureless proton line shape to detect component motions and could distinguish segmental and methyl motion in favorable cases, such as polypropylene, polyisobutylene, and natural rubber.[1] Spin–lattice relaxation times of the protons, T_1(H), could be measured to differentiate between the same motions in poly(isobutylene).[2] Spin–lattice relaxation in the rotating frame, $T_{1\rho}$(H), was found to be a useful parameter in mapping low-frequency motions (tens of kHz) in polymers[3] including poly(propylene oxide).[4] The subject of NMR in solid polymers has been reviewed.[5,6] Several studies are of special relevance to our work. In particular

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