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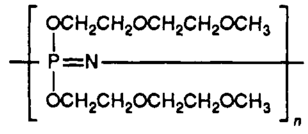
Communications to the Editor

Synthesis and Properties of Polyphosphazene Interpenetrating Polymer Networks

Interpenetrating polymer networks (IPNs) are attracting increasing attention as materials with new or improved physical or mechanical characteristics.[1] The unusual and often unique properties of IPNs are a consequence of both their cross-linked supermolecular structure and their multicomponent nature. In particular, IPNs allow access to properties that may be hybrids of those of the component macromolecules.

Poly(organophosphazenes) are a broad, novel class of inorganic/organic macromolecules, the properties of which may be tailored by the choice of side groups.[2] This has led to applications as biomaterials and oil-resistant elastomers.[3] However, despite patent reports of biomedical uses of polyphosphazene IPNs,[4] to our knowledge, no systematic studies have been reported in the open literature.

As part of our program to synthesize new materials with hybrid macromolecular properties, we report the synthesis of the first, well-characterized interpenetrating polymer networks involving polyphosphazenes and organic polymers. In our initial studies, we have used poly[bis((methoxyethoxy)ethoxy)phosphazene] (MEEP, 1) as the cross-linked polymer matrix. MEEP is a hydrophilic, water-soluble material with little resistance to viscous flow.[5] However, following exposure to ^{60}Co γ-radiation, cross-linking occurs to afford an insoluble gel with increased dimensional stability.[6]



$$\left[-\overset{\displaystyle OCH_2CH_2OCH_2CH_2OCH_3}{\underset{\displaystyle OCH_2CH_2OCH_2CH_2OCH_3}{P}}{=}N- \right]_n$$

1

In a typical experiment, a sample of radiation-cross-linked 1 was allowed to swell in a mixture of methyl methacrylate monomer, an initiator (AIBN), and a cross-linking agent (ethylene glycol dimethacrylate) during 2 days in the absence of light.[7] During this time, an approximate tenfold increase in volume occurred. The swollen matrix was then heated at 70 °C for 8 h to yield the full PMMA/MEEP IPN (2) as a glassy, slightly adhesive material. Purification of 2 from unreacted reactants and soluble products was achieved by drying under vacuum and Soxhlet extraction with THF over 2 days. A similar method was used to synthesize the full polystyrene (PS)/MEEP IPN (3), except that benzoin methyl ether was used as the initiator and divinylbenzene as the cross-linker. In contrast to species 2, IPN 3 was a nonadhesive, flexible material.

The IPNs 2 and 3 were characterized by infrared spectroscopy, ^{1}H and ^{31}P NMR spectroscopy, and differential scanning calorimetry.[8,9] The infrared spectra of 2 and 3 showed the expected absorptions for the component macromolecules. For example, the infrared spectrum of 2 showed a carbonyl band at 1720 cm^{-1} assigned to the PMMA and a broad absorption at ca. 1200 cm^{-1} which was assigned to the P=N skeletal vibrations of 1. The ^{1}H and ^{31}P NMR spectra of 2 and 3 were determined by using swollen gels in CDCl$_3$. The ^{1}H NMR spectra contained the expected, but extremely broad resonances for the component polymers. The ^{31}P NMR spectra of 2 and 3 contained broadened, singlet resonances assigned to cross-linked 1. An analysis of the DSC thermograms of 2 and 3 provided important information about the IPN microstructure. The thermogram of 2 showed glass transition temperatures (T_g's) for the component polymers at +112 (PMMA) and −80 °C (1). The DSC thermogram of 3 (Figure 1) also showed two thermal transitions corresponding to the component polymers, but, in this case, the T_g's were significantly shifted from the values found in the homopolymers. Thus, thermal transitions at +57 and −70 °C were detected, which were assigned to polystyrene and to 1, respectively. This indicates that a significant degree of intimate mixing of the component polymer molecules is present in the matrix. The presence of interchain mixing in 3 is an interesting result, since recent work in our laboratory has shown that polystyrene forms incompatible mixtures rather than compatible blends with 1.[10]

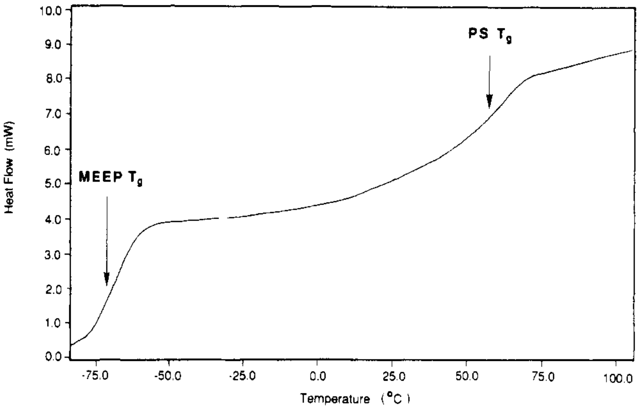


Figure 1. DSC thermogram of IPN 3.

IPNs 2 and 3 represent the first examples of well-characterized interpenetrating polymer networks based on the phosphazene polymer system. More detailed investigations of the microstructures of 2 and 3 together with an exploration of synthetic routes to IPNs derived from polyphosphazenes and other organic or inorganic polymers are in progress.

Acknowledgment. We thank the U.S. Public Health Service through the National Heart, Lung and Blood Institute for support of this work.

References and Notes

(1) (a) Sperling, L. H. *Interpenetrating Polymer Networks and Related Materials*; Plenum Press: New York, 1981. (b) Sperling, L. H. *CHEMTECH.* **1988**, 104.

(2) (a) Allcock, H. R. *Chem. Eng. News* **1985**, *63* (11), 22. (b) Allcock, H. R. *Angew. Chem.* **1977**, *16*, 147. (c) Allcock, H. R. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symp. Ser. 360; American Chemical Society: Washington, DC, 1988.

(3) Penton, H. R. In *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symp. Ser. *360*; American Chemical Society: Washington, DC, 1988; pp 272–282.

0024-9297/90/2223-4885$02.50/0

(4) See, for example, U.S. Patents 4,543,379, 4,661,065, and 4,432,730.

(5) Blonsky, P. M.; Shriver, D. F.; Austin, P. E.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854.

(6) (a) Allcock, H. R.; Kwon, S.; Riding, G. H.; Fitzpatrick, R. J.; Bennett, J. L. *Biomaterials* **1988**, *9*, 509. (b) Allcock, H. R.; Fitzpatrick, R. J.; Gebura, M.; Kwon, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 321.

(7) In a specific example, a sample of **1** (0.1 g) cross-linked with 3 Mrad of ^{60}Co γ-radiation was allowed to swell in 20 mL of a mixture of methyl methacrylate, AIBN initiator, and ethylene glycol dimethacrylate cross-linker for 2 days. The monomers and cross-linkers were purified by distillation and stored under N_2 in the absence of light. After the curing step, the yield of **2** was 0.5 g.

(8) For IPN **2**: ^{1}H NMR δ 0.85, 0.98 (CH_2 of PMMA), 1.85 (Me of PMMA), 3.65 (CO_2Me of PMMA and OCH_2 of 1); ^{31}P NMR δ −10.8; IR 2900 (C–H of PMMA and 1), 1720 (C=O of PMMA), 1200 cm^{-1} (P=N of 1).

(9) For IPN **3**: ^{1}H NMR δ 1.25, 1.65 (CH of PS), 3.38, 3.52, 3.65, 4.05 (OCH_2 of 1), 7.2 (Ph of PS); ^{31}P NMR δ −8.3; IR 3000 (C–H), 1670, 1590 (C=C aromatic), 1200 cm^{-1} (P=N).

(10) PMMA and MEEP also form incompatible blends: Allcock, H. R.; Visscher, K. B., unpublished work.

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