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### A Novel Simultaneous Semi-Interpenetrating Polymer Network of Crosslinked Poly(Methyl Methacrylate) and Poly(2-Benzyl-2-Oxazoline)

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# A NOVEL SIMULTANEOUS SEMI-INTERPENETRATING POLYMER NETWORK OF CROSSLINKED POLY(METHYL METHACRYLATE) AND POLY(2-BENZYL-2-OXAZOLINE)

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## ABSTRACT

The simultaneous cationic, ring-opening polymerization of 2-benzyl-2-oxazoline (BOX) with methyl tosylate in the presence of free-radical (benzoyl peroxide) initiated polymerization of methyl methacrylate (MMA), using ethylene glycol dimethacrylate (EGDMA) crosslinker produced transparent semi-interpenetrating polymer networks (semi-IPNs) with one glass transition temperature ( $T_g$ ), as shown by differential scanning calorimetry (DSC). The MMA/BOX ratios evaluated in the study were 70/30, 50/50, and 30/70. The simultaneous, free-radical, and cationic polymerization of MMA and 2-benzyl-2-oxazoline mixtures, without EGDMA and over the same monomer mixture ratio range, produced opaque plastics with two  $T_g$  values, with both the PMMA and PBOX homopolymers soluble. The  $T_g$  values of the two separated linear polymers were close to those previously reported for the two polymers. Over the monomers mixture range examined, the results clearly show that the simple blend of the PBOX and PMMA polymers are immiscible and that the PBOX/MMA polymers are miscible in the semi-IPN systems. Along with providing a new direction for IPN studies, the novel

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semi-IPNs of the type described may have utility in a variety of applications.

## INTRODUCTION

Interpenetrating polymer networks (IPNs) are more or less intimate mixtures of two or more distinct crosslinked polymers mutually held together by permanent entanglements [1-3], containing essentially no covalent bonds or grafts between the two polymers. If only one of the polymers in any IPN is crosslinked, the material is referred to as a semi-IPN. Semi-IPNs normally exhibit varying degrees of phase separation, but they can show improved morphologies together with thermoplastic processability [4]. A simultaneous semi-IPN can be made by combining two polymers with one of them cured or crosslinked in the presence of the other [5-7] or by mixing two monomers which may be polymerized, with one of the polymeric materials being crosslinked during formation, by different mechanisms, e.g., chain-growth or step-growth polymerization.

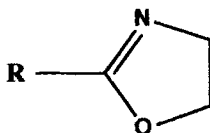
2-Substituted-2-oxazolines (Fig. 1) are interesting compounds which have received considerable attention in recent years [8] for the production of both chain-growth and step-growth polymers or thermosets [9-11].

Oxazoline-based monomers and polymers are known to be highly versatile for a wide spectrum of applications, such as the design of improved coatings and adhesives, specialty chemicals for pharmaceuticals, textile, and paper agents, and compatibilizers [4, 12]. However, as far as we have determined, polyoxazolines used as components of IPNs have received no attention or been reported. In this communication we report on the synthesis of a novel, transparent semi-IPN of crosslinked poly(methyl methacrylate) (PMMA, free-radical polymerization) and poly(2-benzyl-2-oxazoline) (PBOX, cationic ring-opening polymerization) by a simultaneous technique using a solvent-free reaction process. The miscibilities of the two polymers in semi-IPNs and linear blends were examined by differential scanning calorimetry (DSC).

## EXPERIMENTAL

### Materials

Phenylacetonitrile, methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDMA), benzoyl peroxide (BPO), *p*-toluene sulfonate (TsOCH<sub>3</sub>), and zinc acetate were purchased from Aldrich Chemical Co. Ethanolamine (EA) was sup-



R = Alkyl, Aryl, Arylalkyl, etc.

FIG. 1.

plied by Fisher Scientific. All chemicals were used as received. All solvents used were of reagent-grade quality, dried over Linde 4 Å molecular sieves.

### Preparation of 2-Benzyl-2-oxazoline (BOX) Monomer

BOX monomer (Fig. 1, R = benzyl) was prepared via a relatively simple, one-step, high yield procedure, starting from nitriles [13] (Scheme 1).

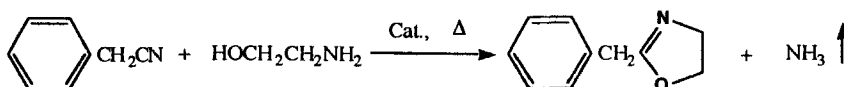
Phenylacetonitrile (1.0 mol) was combined with 1.5 mol of EA, 3.5 g of zinc acetate catalyst (3 wt% of nitrile used), and 300 mL of xylene in a 1000-mL three-neck, round-bottom flask. The flask was fitted with a thermometer, condenser, nitrogen gas inlet tube, magnetic stirrer, and an ammonia gas receiver. The mixture was heated with moderate stirring at the refluxing temperature of xylene (ca. 138°C), under a slow nitrogen stream for 22 hours, until no more ammonia was detected in the off-gas. The excess EA reactant was removed by using a separatory funnel, and xylene was distilled off at 137–139°C. The crude product was purified by distillation twice under vacuum. The final product was a colorless liquid with bp 129°C/2 mmHg, yield 70%. The monomer structure was confirmed by FT-IR, showing a strong  $\text{—C=N—}$  stretching at  $1668\text{ cm}^{-1}$  and  $\text{—C—O—C=}$  at  $1161\text{ cm}^{-1}$ , and  $^1\text{H-NMR}$  spectrum (Fig. 2).

### Preparation of Crosslinked PMMA Network

MMA monomer (3.09 g) was combined with 0.15 g of EGDMA and 0.06 g BPO (2 wt% of MMA) in a clean glass vial. The vial and contents were purged with dry  $\text{N}_2$  for 5 minutes and then tightly sealed. After being shaken 40 minutes in a thermostatted water bath at 23°C, the mixture was still a clear, easy to flow liquid without any visually detected increase in viscosity. The reaction vial and contents were then heated at 70°C for 8 hours; during this time the mixture solidified. The temperature was raised and kept at 130°C for 12 hours. A colorless, transparent, crosslinked PMMA was produced.

### Preparation of Semi-IPNs and Linear Blends

The semi-IPNs were prepared by mixing various w/w ratios of both MMA and BOX in predried, clean glass vials to give various compositions. This was followed by adding the free-radical initiator BPO, the EGDMA crosslinker, and the cationic initiator  $\text{TsOCH}_3$ . The mixture was purged with dry  $\text{N}_2$ , and the glass vial was tightly sealed. After 40 minutes in a thermostatted shaker bath at 23°C, all samples were found to have formed totally transparent gels. The samples were further polymerized by heating for 8 hours at 70°C, followed by heating for 12 hours at 130°C. All semi-IPN products were transparent, brownish yellow, hard



SCHEME 1.

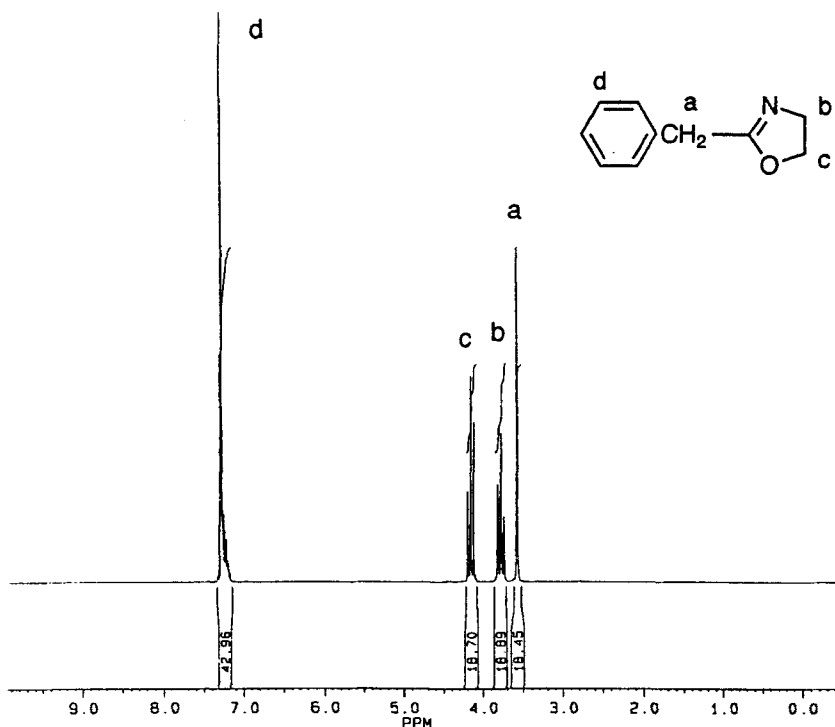


FIG. 2. H-NMR spectrum of 2-benzyl-2-oxazoline (in  $\text{CDCl}_3$ ).

solids. Linear blends of the same compositions as semi-IPNs were also prepared in the same manner as the semi-IPNs except that the crosslinking agent EGDMA for the PMMA was omitted. The linear blends were opaque, pale yellow, hard solids. All the above samples were evaluated by differential scanning calorimetry using a TA Instruments DSC 910 unit programmed under  $\text{N}_2$  over the range 30–180°C at a scanning rate of 20°C/min.

## RESULTS AND DISCUSSION

The results of the DSC measurements for the crosslinked PMMA, semi-IPNs, and linear blends of PMMA/PBOX are listed in Table 1. As shown, the semi-IPNs produced are optically transparent, exhibiting a single glass transition ( $T_g$ ) for each composition. The three linear blends, in comparison, are optically opaque, having  $T_g$  transitions at two temperatures. DSC thermograms of a semi-IPN and a linear blend with the same composition [PMMA/BOX, w/w (50/50)] are shown in Figs. 3 and 4. These results suggest that the two polymers of PMMA and PBOX are miscible in the semi-IPN and immiscible in their linear blends. It has been previously reported that poly(ethyl oxazoline) (PEOX) is immiscible with PMMA in their linear blends [14].

TABLE 1. DSC Measurement Results<sup>a</sup>

Sample	MMA/BOX composition (w/w)	$T_g$	Remarks
PMMA (crosslinked)	100/0	115.7	TP, colorless, hard
PBOX	100/0	61.4	TP, BY, hard
Semi-IPN1	70/30	70.8	TP, BY, hard
Semi-IPN2	50/50	60.1	TP, BY, hard
Semi-IPN3	30/70	65.2	TP, BY, hard
L-Blend1	70/30	57.7, 115.2	OP, PY, hard
L-Blend2	50/50	55.9, 106.8	OP, PY, hard
L-Blend3	30/70	65.1, 118.8	OP, PY, hard

<sup>a</sup>BY = brownish yellow, PY = pale yellow, OP = opaque, TP = transparent.

<sup>b</sup>PMT = 67.9°C.

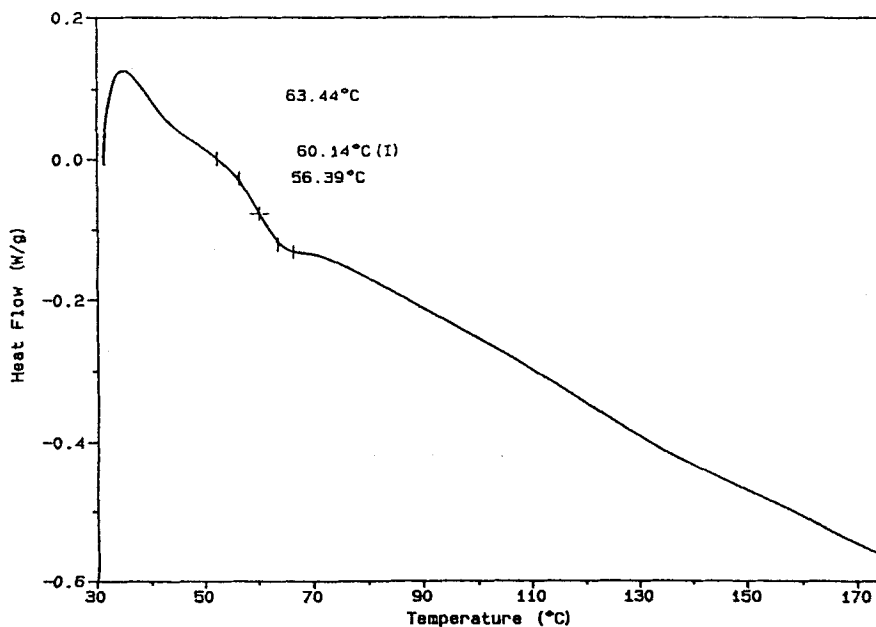


FIG. 3. DSC thermogram of semi-IPN2 [PMMA/PBOX, w/w (50/50)].

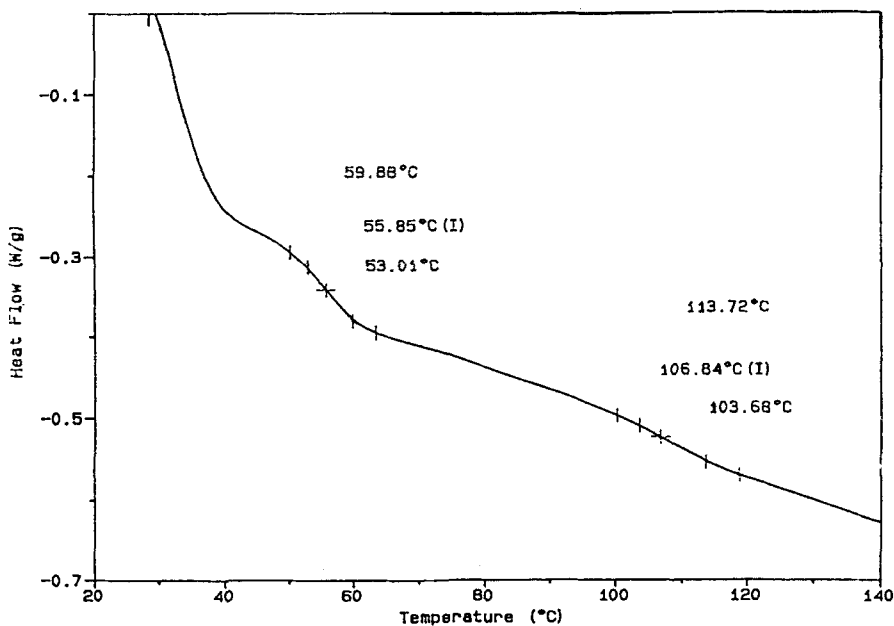
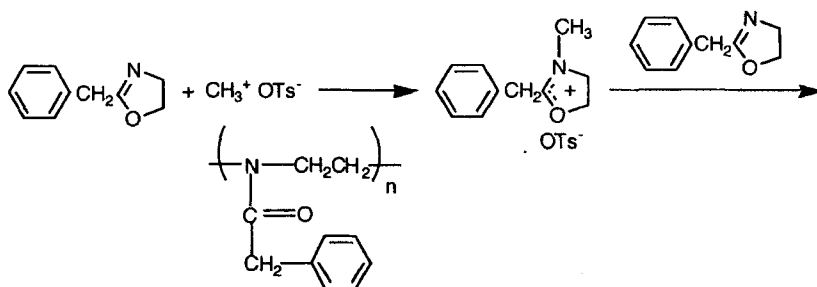


FIG. 4. DSC thermogram of L-blends [PMMA/PBOX, w/w (50/50)].

2-Benzyl-2-oxazoline (BOX) monomer polymerized in the semi-IPNs and linear blends according to a cationic, ring-opening polymerization (Scheme 2) mechanism [15].

Extraction experiments on the ring-opening, cationic polymerized product of Scheme 2 showed that the cationic polymerization reaction did not interfere with the free-radical polymerization/crosslinking of MMA.

No polymerization was found for the MMA monomer types used for the preparation of semi-IPNs and linear blends upon heating the monomers at 80°C for 24 hours using only  $\text{TsOCH}_3$  cationic initiator without BPO. Extraction studies on free-radical polymerized or crosslinked PMMA, semi-IPNs [PMMA/PBOX, w/w (50/50)] and linear blends [PMMA/PBOX, w/w (50/50)], using  $\text{CHCl}_3$  and a Soxhlet extractor, gave results as follows.



SCHEME 2.

1. No weight loss for crosslinked PMMA after extraction and drying.
2. The semi-IPNs sample lost 50 wt% after extraction and the remaining solid retained the appearance and  $T_g$  of PMMA.
3. The linear blends completely dissolved in  $\text{CHCl}_3$  upon extraction.

The extraction results provide evidence that there are no chemical bonds between PMMA and PBOX in the system under study. All the linear chains of PBOX may be extracted from the crosslinked PMMA matrix with suitable solvents. The enhanced miscibility of PMMA with PBOX in semi-IPNs is considered to be fostered by nonpermanent entanglements of the polymer chains. There is no evidence to show covalent chemical bonding was produced between PMMA and PBOX polymers for both the semi-IPN and linear blends. It was also observed that the oxazoline monomer acted as a promoter for the free-radical polymerization of MMA from the gel formation in the early stage of semi-IPN preparation.

The novel semi-IPNs prepared in this work are of possible interest in the preparation of solvent-free coatings, adhesives, composites, and other thermoset systems. Because of the unique functionality and varied chemistries provided by cyclic imino ether (oxazoline and oxazine) moieties, we believe that many more interesting IPN and semi-IPN systems containing the oxazoline and oxazine moieties will be described in future work.

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