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Synthesis and Characterization of Interpenetrating Polymer Networks of Poly(2,6-dimethyl-1,4-phenylene oxide) and Poly(butadiene)

Harry L. Frisch* and Yao-He Hua[†]

Department of Chemistry, State University of New York, Albany, New York 12222.

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ABSTRACT: Full interpenetrating and pseudointerpenetrating networks (IPN's) of poly(2,6-dimethyl-1,4-phenylene oxide) and polybutadiene (PB) were synthesized and characterized. A single, intermediate glass transition temperature (obtained from differential scanning calorimetry) and electron transmission micrographs with no resolvable phase contrast to magnifications of 55 300 are found for the full IPN's over the whole composition range. Thus, unlike the linear blends, the full IPN's do not exhibit microphase separation. Except for the 10% by weight linear PB pseudo-IPN all other pseudo-IPN's are opaque and exhibit two glass transition temperatures and appear to have phase separated. The full IPN's exhibit a maximum tensile stress to break around 10% by weight PB and a maximum in elongation to break at 80% by weight PB.

Introduction

Interpenetrating polymer networks (IPNs)[1-6] are more or less intimate mixtures of two or more distinct cross-linked polymers mutually held together by permanent entanglements, containing essentially no covalent bonds or grafts between them. IPNs exhibit varying degrees of phase separation, dependent principally on the compatibility of the polymers. With highly incompatible polymers, the thermodynamic forces leading to phase separation are so powerful that only limited gains in phase mixing, for example, only an extended homogeneous range of composition, occur. In cases where the polymers are more compatible, phase separation can be almost completely circumvented. Compatibility of the linear polymers is not necessary to achieve complete phase mixing, since the permanent entanglements (catenation) can effectively prevent phase separation.[7] With intermediate situations of compatibility, more complex behavior can result. Thus IPN's with dispersed phase domains ranging from a few micrometers (incompatible) to a few tens of nanometers (intermediate) and finally to those with no resolvable domain structure (complete mixing)[8-10] have been reported.

In the present study, we have synthesized and investigated the physical properties and morphology of IPNs of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polybutadiene (PB), as part of an ongoing study of IPN's of PPO with other polymer networks. The overall solubility parameter of linear PPO, $\delta = 9.1\ (\mathrm{cal/cm^3})^{1/2}$, differs significantly from that of PB, $\delta = 8.4\ (\mathrm{cal/cm^3})^{1/2}$, and there is a difference of about 300 °C in their glass transition temperatures. The major purpose of this study is to show that single-phase (over all compositions) IPN's with improved properties can be made from components whose linear blends are completely incompatible.

Experimental Section

Materials. The raw materials used and their descriptions are listed in Table I. EDA was distilled at 55-60 °C in a stream of nitrogen under vacuum. EGDMA was washed with 10% aqueous sodium hydroxide and then distilled at 35-40 °C under vacuum of about 2 mmHg; BPO was dissolved in carbon tetrachloride, precipitated, washed with cool methanol, and then dried at room temperature under a vacuum of about 2 mmHg. All solvents were dried over Linde 4A molecular sieves. NBS was used without further purification.

Table I

designation	description	source
PPO	poly(2,6-dimethyl-1,4-phenylene oxide) M_w = 43 560, solubility param $\delta = 9.1\ (\mathrm{cal/cm^3})^{1/2}$, $\rho = 1.06\ \mathrm{g/cm^3}$	General Electric Co.
PB	polybutadiene, cis and trans, $M_w = 2 \times 10^5$-3.3×10^5, solubility param $\delta = 8.38\ (\mathrm{cal/cm^3})^{1/2}$, $\rho = 0.90\ \mathrm{g/cm^3}$, $T_g = -95$ °C	Aldrich Chemical Co.
NBS	*N*-bromosuccinimide, reagent	Aldrich Chemical Co.
EDA[a]	ethylenediamine, reagent	Aldrich Chemical Co.
EGDMA	ethylene glycol dimethacrylate, reagent	Aldrich Chemical Co.
BPO	benzoyl peroxide, reagent	Aldrich Chemical Co.
	chloroform, reagent	MCB Manufacturing Chemicals, Inc.
	carbon tetrachloride, reagent	Fisher Scientific
	toluene, reagent	Fisher Scientific
	methanol, reagent	Fisher Scientific

[a] EDA was distilled at 55-60 °C in a stream of nitrogen under vacuum. EGDMA was washed with 10% aqueous sodium hydroxide and then distilled at 35-40 °C under vacuum.

Preparation of Polymers and IPNs. A. Bromination of PPO.[11] PPO received from General Electric Co., which had M_w = 43 560 determined by light scattering and M_n = 13 390 by vapor-phase osmometry, was purified by dissolving it in chloroform and precipitating it with methanol and dried. The purified PPO was brominated with NBS in the solution of carbon tetrachloride. Carbon tetrachloride (1.5 L), 144 g (1.2 mol) of purified PPO, and 21.4 g (0.12 mol) of NBS were combined in a 2-L, round-bottomed, three-necked flask equipped with a mechanical stirrer, thermometer, condenser, and nitrogen inlet. The reaction mixture, maintained under a nitrogen atmosphere and illuminated with 100-W flood lamp, was stirred and heated at 50 °C for 3 h. The brominated PPO (Br-PPO) was precipitated with methanol, filtered, and washed with methanol. The material was purified by dissolving it in toluene and precipitating it with methanol, then it was washed several times with methanol and dried in an oven at 70 °C for 36 h.

B. Preparation of Cross-Linked PPO. Br-PPO (4 g) was dissolved in 40 mL of toluene. To the solution was added 0.04 g of ethylenediamine. The solution was vigorously stirred at 60 °C for 10 min, degassed, poured into a Petri dish, placed in an oven at 70 °C for 48 h and 90 °C for 3 h, and then heated at 60 °C under vacuum to remove excess solvent. The sample was kept in a desiccator under vacuum before testing. The number-average molecular weight between two cross-links M_e of the PPO network

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[†] Permanent address: Jiagnsu Province Research Institute of Chemical Technology, 72 West Beijing Road, Naijing, The People's Republic of China 20024.

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Table II
Results of Measurements on the Full IPNs

sample	comp, wt % PPO–PB	color, transparency[a]	tensile strength, psi	elongation to break, %	T_g, °C
cross-linked PPO	100–0	PY, TP	5890	2.95	210
FIPN 10	90–10	PY, TP	6434	4.99	205
FIPN 20	80–20	PY, TU	5251	3.73	206
FIPN 30	70–30	PY, TU	4530	3.47	199
FIPN 40	60–40	PY, TU	1871	3.33	71
FIPN 50	50–50	PY, TU	943	2.0	59
FIPN 60	40–60	PY, TU	124	5.6	−14
FIPN 80	20–80	PY, TU	~75	>87	−82
cross-linked PB	0–100	PY, TU	7	31.4	−85

[a] PY = pale yellow, TP = transparent, TU = translucent.

Table III
Results of Measurements onthe Pseudo-IPNs

sample	comp, wt % PPO–PB	type of PPO	type of PB	color, transparency[a]	T_g, °C
PIPN 10	90–10	cross-linked	linear	PY, TP	181
PIPN 30	70–30	cross-linked	linear	PY, OP	0.211
PIPN 50	50–50	cross-linked	linear	PY, OP	−7, 217
PIPN 60	40–60	linear	cross-linked	PY, OP	−14, 209
PIPN 80	20–80	linear	cross-linked	PY, OP	

[a] PY = pale yellow, TP = transparent, OP = opaque.

is 3000 from the employed stoichiometry.

C. Preparation of Cross-Linked Polybutadiene. Linear PB (20% cis, 60% trans, and 20% 1,2-addition) was purified by dissolving it in toluene and precipitating it with methanol. After filtration it was washed several times with methanol and dried. Purified PB (4 g) was dissolved in 80 mL of toluene. To the solution was added 0.1 g of EGDMA and 0.02 g of BPO. The reaction procedures were the same as for cross-linked PPO, but the bottom of the Petri dish was covered with a thin layer of clean, dry mercury to prevent adhesion. The M_e of the PB network is 4000 from the employed stoichiometry.

D. Preparation of IPNs. 1. Full IPNs. The full IPN was prepared by dissolving the linear PB and Br-PPO in toluene (4 g of polymers in 48–72 mL of toluene, depending on composition), plus BPO, EGDMA, and EDA. The vigorously stirred solution was heated for 10 min at 60 °C and was clear. It was degassed and poured into a Petri dish, which was placed in an oven at 70 °C for 48 hours and 90 °C for 3 h. Excess solvent was further removed at 60 °C under vacuum for 48 h. The bottom of the Petri dish was covered with a thin layer of clean, dry mercury for those samples with PB content of more than 40% (wt).

2. Pseudo- or Semi-IPNs. The semi-IPNs were prepared by dissolving the linear PB and Br-PPO in toluene, plus ethylenediamine or EGDMA/BPO. The reaction conditions were the same as those for the full IPNs.

Measurements. A. Ultimate Properties. The tensile strength (TS) and elongation at break were measured at room temperature on an Instron Tester (ASTM Di708) with cross-head speed of 2 in. per min. Specimens were 0.25-in.-wide dumbbells.

B. Electron Micrographs. The samples were prepared according to Kato's osmium tetraoxide technique and a two-step sectioning method. The electron micrographs were taken at magnifications varying from 55 300 to 8800 with a Phillips 300 transmitting electron microscope.

C. Differential Scanning Calorimetry (DSC). The glass transition temperatures were determined on a DSC V2.2A Du Pont 9000 differential scanning calorimeter. Measurements on 10-mg samples were carried out from −110 to 260 °C under nitrogen at a scanning rate of 20 °C/min.

Results and Discussion

The IR spectra of PPO, Br-PPO, PB, cross-linked PPO, cross-linked PB, and full IPNs were obtained and the results were in accord with the expected structures.

The mechanical and thermal properties if the IPNs listed in Tables II and III. The transparency was estimated for the 0.25-mm-thick samples.

Transmission electron micrographs (TEM) of the full IPNs of 20%, 40%, and 50% polybutadiene showed no resolvable contrast in transmission electron density up to magnifications of 55 300. In accordance with the TEM, all full IPN samples exhibit a single glass transition temperature in between the T_g values of the pure cross-linked PB and PPO. But only the pseudo-IPN of 10% linear PB has a single T_g behavior. Phase separation occurred in all other pseudo-IPN's when the rubber content was more than 30% by weight.

The PPO/PB full IPNs exhibit not only a maximum in the tensile stress to break (around 10% PB) but also a maximum in the elongation to break (around 80% PB). We speculate that the 10% by weight of PB composition may reflect a maximum extent of catenation of the two networks.[11] The elongation to break begins increasing apparently as the T_g decreases to below room temperature (around 60% PB).

Conclusions

The simultaneous full IPN's of PPO and PB, over the whole composition range, have only one T_g, which together with the electron microscopy results suggests a single-phase morphology, even though their linear polymer blends are completely incompatible. A maximum in the tensile stress to break and a maximum in the elongation to break were observed. This maximum in tensile stress to break composition is also observed with IPN's of PPO with polystyrene,[11] poly(methyl methacrylate),[12] and poly(dimethylsiloxane).[13]

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Registry No. PPO (SRU), 24938-67-8; PPO (homopolymer), 25134-01-4; PB, 9003-17-2.

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Properties of Aromatic Copolyesters Derived from *p*-Hydroxybenzoic Acid, Terephthalic Acid, and Naphthalenediol Isomers

Jung-Il Jin*,† **and Jin-Hae Chang**†,‡

Chemistry Department, College of Sciences, Korea University, 1-Anam Dong,
Seoul 136-701, Korea, and Polymer Science and Engineering Department, Kum-Oh
Institute of Technology, Gumi City 730-070, Korea

Hong-Ku Shim

Chemistry Department, Korea Institute of Technology, Daejon City 301-338, Korea.

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ABSTRACT: A series of aromatic copolyesters were prepared in the melt from terephthalic acid (TPA), *p*-acetoxybenzoic acid (ABA), and diacetoxynaphthalene (DAN) isomers. The DAN isomers used in this study were the 1,4-, 1,5-, 1,6-, 1,7-, 2,3-, 2,6-, and 2,7-derivatives. All the polymers having the composition (molar ratio) of TPA:DAN:ABA = 1:1:2 are thermotropic, while some of the compositions derived from a lower concentration of ABA are not mesomorphic. All as-polymerized samples, except those prepared from 2,6- and 2,7-DAN, are amorphous. Their glass transition temperatures (T_g) ranged from about 80 to 145 °C, depending on the polymer composition and the structure of the naphthylene unit. The melting temperatures (T_m) of the 2,6-DAN copolymers were about 260 °C, while those of 2,7-DAN copolymers ranged from 190 to 245 °C, depending on the content of the *p*-oxybenzoyl unit. Annealing increased copolymer molecular weights and also the degree of crystallinity of crystallizable compositions. Most of the thermotropic copolymers formed nematic phases, while 1,4- and 1,5-DAN copolymers formed smectic phases.

Introduction

The importance of thermotropic aromatic polyesters as a new class of materials is ever increasing because in their liquid-crystalline state they can be spun or injection molded, leading to oriented fibers or plastics of high strength.[1-4] One of the most distinguishing properties of these polymers is the ease in producing a uniform molecular orientation by the elongation flow experienced during processing or intentionally applied. Such a molecular orientation not only gives rise to high strength but also results in low melt viscosity along the flow direction.

The two representative linear, aromatic polyesters, poly(*p*-phenylene terephthalate) and poly(*p*-hydroxybenzoate), however, are too high melting to be melt processed. Various structural and compositional modifications have produced numerous low-melting homo- and copolyesters that could be readily processed and characterized. Inclusion of flexible spacers or nonlinear structural elements and copolymerization are the most frequently utilized synthetic approaches. The presence of unsymmetrical, bulky substituents on phenylene rings also is very effective in reducing T_m.[5] But many of the resulting polymers no longer possess the desirable properties, such as liquid crystallinity and linearity and rigidity of the chain, which are necessary to attain superior mechanical properties.

In one of our earlier papers[6] we reported the loss of liquid crystallinity by incorporation of nonlinear bis(phenol) structures in the polyesters based on terephthalic acid and 2-chlorohydroquinone. Properties of aromatic polyesters derived from 2-bromo- or 2-nitroterephthalic acid and a series of unsymmetrically substituted hydroquinones also were investigated by us.[7] Structure–property relationships of main-chain, thermotropic polyesters having on alternating sequence of mesogenic units and aliphatic, flexible spacers are subjects of many of our earlier studies.[8-10] In this investigation we prepared a series of aromatic copolyesters at three different molar ratios of terephthalic acid (TPA), *p*-acetoxybenzoic acid (ABA), and diacetoxynaphthalene (DAN) isomers. The DAN isomers included are the 1,4-, 1,5-, 1,6-, 1,7-, 2,3-, 2,6-, and 2,7-derivatives. The molar ratio of TPA and DAN was kept

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† Korea University.

‡ Kum-Oh Institute of Technology.

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