observed over a wide range of 220–600 nm in uv and visible spectra. On the other hand, in the poly(phenylpropyne) the maximum absorption was observed at 230 nm. ϵ_{max} was ca. 7000, and no absorption existed in a range where wavelength is greater than 380 nm. These results support that the polyenes of poly(phenylpropyne) are not in the conjugated state due to the steric effect of two bulky groups, methyl and phenyl.

In conclusion, phenylpropyne was polymerized by $WCl_6 \cdot Ph_4Sn$ to a polymer with a molecular weight of several thousand, and the polymer obtained was linear and possessed methyl and phenyl side groups.

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The Reaction of Polyoxyethylene Glycols with Epichlorohydrin. Factors Affecting the Composition and Yield of Volatile Products

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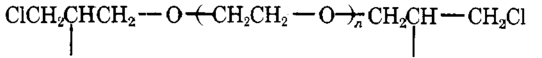
ABSTRACT: The side reactions which accompany the addition of α-hydro-ω-hydroxypoly(oxy-1,2-ethanediyl) (I) (average molecular weight of 588 and 1480) to epichlorohydrin (ECH) catalyzed by boron trifluoride etherate have been studied. Dioxane arises solely from I while the other products, identified as *cis*- and *trans*-4-chloromethyl-2-methyl-1-3-dioxolane (CMMD) and 2-chloromethyl-1,4-dioxane (CMD), are derived from both I and ECH. Various additives, water, 3-chloro-1,2-propanediol, 1,4-butanediol, and tetrahydrofuran, were evaluated for effectiveness in reducing the formation of volatile products. Only water proved effective at the levels tested. With I of molecular weight 1480, and no water added, about 14–16% dioxane was produced. With 1–1.5% water dioxane was reduced to 3–4% with corresponding reductions in CMD but not in CMMD. CMMD can be produced from I, 3-chloro-1,2-propanediol, and catalyst even when no ECH is present. Although dioxane is suppressed when water is present, the average molecular weight of the adduct is less than that of the starting material.

The cationic polymerization of ethylene oxide catalyzed by boron trifluoride etherate produces substantial quantities of 1,4-dioxane as well as α-hydro-ω-hydroxypoly(oxy-1,2-ethanediyl) (I), hereinafter referred to as "polyoxyethylene glycol" (POEG).[1] In addition, POEG will, in the presence of ethylene oxide and the catalyst, partially depolymerize to yield dioxane and some 2-methyl-1,3-dioxolane. A subsequent study showed that the depolymerization of POEG to yield dioxane without the formation of 2-methyl-1,3-dioxolane can be effected by the addition of triethyloxonium fluoroborate with neither ethylene oxide nor boron trifluoride etherate being present.[2]

Alcohols, including POEG, react with 1-chloro-2,3-epoxypropane (epichlorohydrin, ECH) in the presence of boron trifluoride etherate[3] to yield, in the case of POEG, useful products such as II



$$ClCH_2\underset{OH}{\underset{|}{C}}HCH_2-O\!\left(CH_2CH_2-O\right)_n CH_2\underset{OH}{\underset{|}{C}}H-CH_2Cl$$

II

having end groups capable of being converted into the epoxide function. The purpose of this investigation was to determine the nature and quantity of volatile products formed in the POEG–ECH reaction catalyzed by boron trifluoride etherate. For the purposes of this study, volatile products were defined as those materials which can be stripped from the neutralized reaction mixture at 115 °C and 2 Torr.

Results and Discussion

Nature of the Volatile Products. The earlier work[1] with POEG, ethylene oxide, and boron trifluoride etherate revealed the presence of dioxane and 2-methyl-1,3-dioxolane, both of which might arise either from the polymer, or from ethylene oxide, or from both. In the reaction with ECH dioxane must arise solely from the POEG and any products containing chlorine must arise, at least in part, from ECH. The volatile product from a typical run was analyzed by GLC and was found to consist of five substances: dioxane, a trace of ECH, and three substances with longer retention times than ECH. Peaks 3 and 4 were close together and the fifth and last peak emerged several minutes later.

GLC–mass spectrometric analysis showed that the substances responsible for peaks 3, 4, and 5 all had parent masses of 136 and contained one chlorine atom. Peaks 3 and 4 together had fragmentation patterns different from that of peak 5. NMR spectra for gas chromatographic fractions repre-

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Table I
Effect of Six Variables in the POEG/ECH Reaction[a]

Output	GMCH[b]	Water[c]	BD[b]	Mol wt[d]	Time[e]	Temp[f]
(1) % wt volatiles basis POEG + ECH + volatile additives	0	−	0	0	0	0
(2) % wt volatiles basis POEG	0	−	0	−	0	0
(3) Dioxane/volatiles, ratio of GLC peak areas	0	−	0	0	0	0
(4) CMD/volatiles, ratio of GLC peak areas	0	0	0	−	0	0
(5) CMMD/volatiles, ratio of GLC peak areas	0	+	0	0	0	+

[a] "+" indicates a significant *increase* in the output with an *increase* in the variable. "−" indicates a significant *decrease* with an *increase* in the variable. "0" indicates no significant effect at the levels of variables chosen. [b] High, 1–1.2% wt basis POEG; low, 0%. [c] High, 1.2% wt basis POEG, low 0%. [d] High, 1480; low, 588. [e] High, 4 h; low, 2 h. [f] High, 80 °C; low, 60 °C.

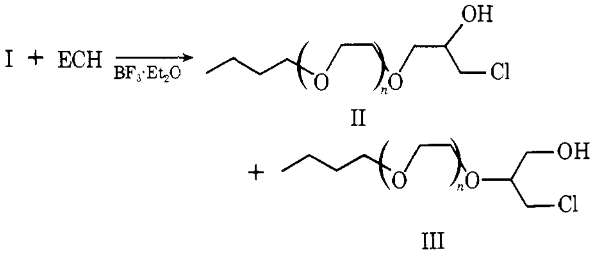
senting peaks 3 and 4 revealed that these peaks were respectively *cis*- and *trans*-4-chloromethyl-2-methyl-1,3-dioxolane[4] (CMMD). Peak 5 was suspected to be 2-chloromethyl-1,4-dioxane[5] (CMD) and an NMR spectrum of the GLC fraction confirmed this. Authentic samples of CMD and a mixture of *cis*- and *trans*-CMMD were prepared and the chromatograms, NMR spectra, and mass spectra agreed in every particular with those of material obtained from an actual run. It is clear then that dioxane must arise only from depolymerization of POEG and that CMMD and CMD are each derived in part from POEG and in part from ECH.

Water was reported[1] to be a suppressant for dioxane formation in the polymerization of ethylene oxide and proved to be in this case as well.

Effect of Conditions on the Yield of Volatile Products. A 12-run Plackett–Berman[6] screening experiment was performed to test the effects of temperature, reaction time, molecular weight of POEG, and three additives: water, 3-chloro-1,2-propanediol (glycerol monochlorohydrin (GMCH)), and 1,4-butanediol (BD) (Table I). At the levels of variables chosen only increased water significantly depressed the level of volatiles formed on the basis of POEG + ECH + volatile additives. Also, on the basis of POEG alone, less volatiles were obtained at higher water concentrations and when POEG of average molecular weight 588 was used. Examination of the ratio of individual volatile products to the total volatiles is revealing. Dioxane is suppressed by water and is unaffected by changes in the other variables at the levels tested. CMD decreases with increasing molecular weight of POEG. A reasonable interpretation of this fact is that CMD is produced by a reaction at the ends of the molecules, and the lower molecular weight polymer, having a higher ratio of ends to chain proper, produces more CMD. The ratio of CMMD to total volatiles increases with water content and with increasing temperature. This could result from a dehydration or cracking reaction which produces a vinyl ether terminus on a polymer chain. Higher temperatures favor such reactions. Water can react with ECH to produce GMCH which, in turn, will react with a vinyl ether to produce CMMD.[7] It could be argued that water hydrolyzes the vinyl ether to acetaldehyde which can react with ECH to form CMMD,[8] but it was found that CMMD was produced in the absence of ECH and added water merely by treating POEG and GMCH with boron trifluoride etherate under reaction conditions. Water is also formed under such circumstances, presumably from the dehydration of polymer chain termini. It was also found that the model compound isobutyl vinyl ether reacts smoothly and rapidly with GMCH to form CMMD when catalyzed either by boron trifluoride etherate or methanesulfonic acid.

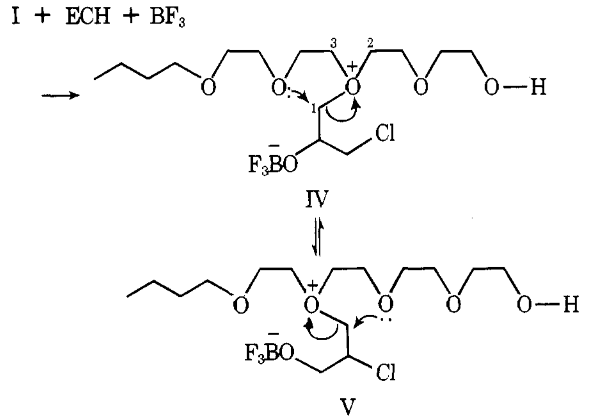
Reactions

Capping. Capping of I may occur to yield the principal product II and lesser amounts of III (reaction 1).



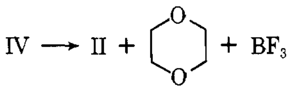
(1)

Formation of Oxonium Ions. In addition to capping reactions the formation of a variety of oxonium ions would be expected[9] and any one of these ions might isomerize by an "oxonium ion walk" reaction (reaction 2).



(2)

Reactions of Oxonium Ions. Consider the oxonium ion IV. Attack by the terminal hydroxyl group on methylene carbon 2 would yield dioxane and a capped POEG shortened by two ethylene oxide units (reaction 3).

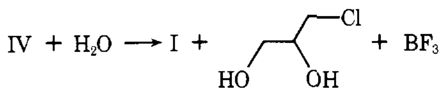


(3)

Attack by the terminal hydroxyl group on methylene carbons 1 or 3 would yield normally capped polymer II with the chain length intact (reaction 4).

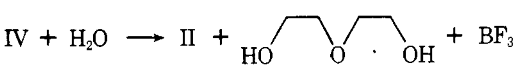
$$IV \longrightarrow II + BF_3 \qquad (4)$$

Attack by a water molecule on methylene carbon 1 would yield GMCH and the original polymer I (reaction 5).

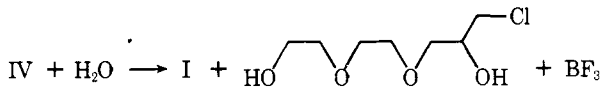


(5)

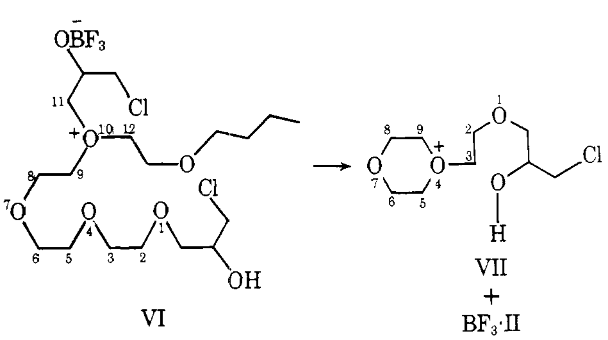
Attack by water on methylene carbon 2 would yield diethylene glycol and normally capped polymer II shortened by two ethylene oxide units (reaction 6).


(6)

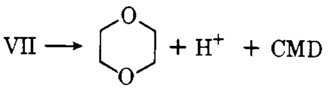
Attack by water on methylene carbon 3 would yield diethylene glycol capped on one end and a new POEG shortened by two ethylene oxide units (reaction 7).


(7)

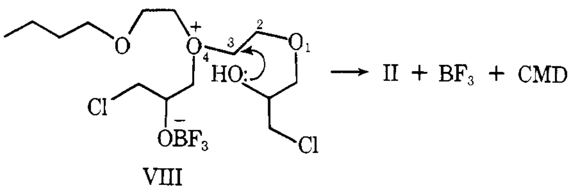
Formation of 2-Chloromethyl-1,4-dioxane (CMD). Consider the structure VI in which capped POEG has undergone oxonium ion formation at oxygen atom 10. Nucleophilic attack by oxygen atom 4 on methylene carbon 9 would yield capped polymer II shortened by three ethylene oxide units and the fragment VII (numbered as in VI) (reaction 8).


(8)

Attack by the hydroxyl group of VII on methylene carbon 3 (a highly favorable pseudo-six-membered ring transition state) would yield both dioxane and CMD (reaction 9).[11]


(9)

Alternatively, oxonium ion VIII (numbered as in VI) might form CMD by attack by the hydroxyl group on methylene carbon 3 with release of capped polymer II shortened by one ethylene oxide unit (reaction 10).


(10)

Formation of *cis*- and *trans*-4-Chloromethyl-2-methyl-1,3-dioxolane (CMMD). The evidence suggests that some kind of dehydration reaction, perhaps (11), can produce a chain with a vinyl ether terminus, X, which might then react rapidly with GMCH, formed by hydrolysis of ECH, to form CMMD and I shortened by one ethylene oxide unit (reaction 12).

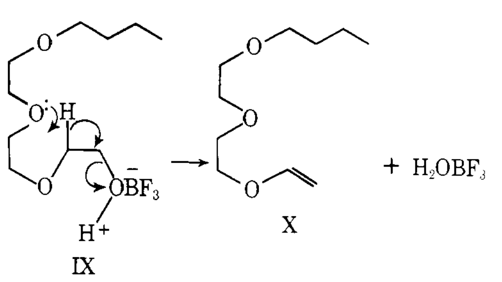
The reactions depicted above are not intended to be an exhaustive cataloguing of every conceivable process which might occur. Rather, they are intended to show, by reactions which have precedent,[2,9,10] how the products found in this reaction might arise.

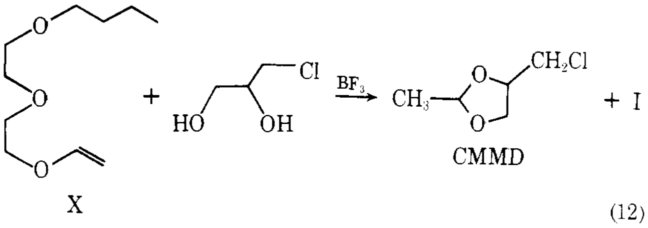
When dioxane formation is suppressed by the presence of water, shorter chains would result if reactions such as 6 and 7 occur. GMCH could also be produced by hydrolysis either of ECH[12] or of oxonium ions (reaction 5) and, if formed while there is still unreacted ECH present, would be at least partially capped by ECH to form a product which would not be volatile. The presence of shorter chains in the product of "wet" runs is evident (Table II). In those runs which were dry, the average molecular weight, as determined by hydroxyl number, remained high (>1250) even at dioxane production as high as 15.6%. In runs with added water average molecular weights were <910. Especially in the case (run No. 6) where extra ECH was added to compensate for the OH groups of water, the lowest molecular weight of all was obtained. It is thus evident that while dioxane formation can be suppressed by adding water to the reaction mixtures, the polymer chains are shortened on the average. Chain shortening is also seen in the results of molecular weight distribution determination by gel permeation chromatography (Figure 1). Adduct from a run at 1.2% water has 8% material with a molecular weight of <400 compared to none for the starting material and 6% for a run with no added water, despite the fact that only 3.3% dioxane was formed in the run with 1.2% water and 15.6% dioxane was obtained in the run with no water. Not much effective chain lengthening occurs, e.g., by chain transfer (attack by POEG hydroxyl on methylene carbons 2 or 3 of IV), as evidenced by the lack of significant quantities of adduct of substantially higher molecular weight than the starting material.

Table II
Reaction of POEG[a] with ECH[e]

Run No.	Water, %	Mol wt[b]	ECH/OH[c]	% dioxane[d]
1	0	1272	1.2	15.6
2	0	1285	1.0	8.8
3	0	1442	0.82	6.2
4	1.0	863	0.66	3.9
5	1.2	903	0.60	3.3
6	1.2	744	1.11	12.8
7	1.6	834	0.51	2.7
8	1.6	849	0.51	2.4
9	GMCH, 7.4%	888	0.58	6.9
10	THF, 5%	1420	1.2	11.3

[a] Mol wt = 1480. [b] Determined from the hydroxyl number. [c] Based on the OH groups in the POEG plus those in water. Water was considered to have two OH groups. [d] Wt % basis POEG + ECH + water. [e] Effect of water on the molecular weight of the adduct and dioxane formation.


(11)



Experimental Section

Materials Used. α-Hydro-ω-hydroxypoly(oxy-1,2-ethanediyl) (I). Commercial products of the BASF Wyandotte Corporation were used: PLURACOL E-1500 average molecular weight of 1480 (as determined by hydroxyl number[13]), and PLURACOL E-600, average molecular weight 588.

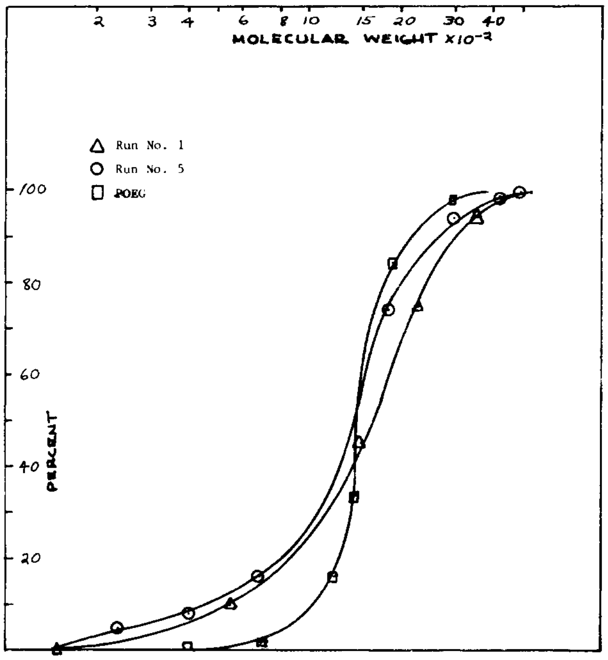


Figure 1. Molecular weight distribution of POEG and POEG/ECH adducts.

Boron trifluoride etherate, as supplied by Aldrich Chemical Co., was used without further purification.

3-Chloro-1,2-epoxypropane, as supplied by Matheson Coleman and Bell, was used without further purification.

3-Chloro-1,2-propanediol, supplied by Aldrich Chemical Co., was distilled and the material boiling at 82–85 °C (1 Torr) was collected.

1,4-Butanediol, supplied by General Aniline and Film, was distilled and the material boiling at 88 °C (2 Torr) was retained.

Isobutyl vinyl ether, supplied by General Aniline and Film, was used without further purification.

General Procedure

The reactions were run in a 1-l. round-bottomed flask equipped with a stirrer, thermometer, condenser with drying tube, and a pressure equalized dropping funnel. Molten POEG was placed in a weighed flask and dried by stirring at 110 °C (2 Torr) for ½ h. The catalyst, boron trifluoride etherate, 0.2% by weight, was premixed with the additives, if any, and added to the POEG at the appropriate temperature (60 or 80 °C). The required amount of epichlorohydrin was added over a 10-min period by means of the dropping funnel which was replaced by a plug after addition was complete. The temperature was maintained (±2 °C) by external cooling or heating. At the conclusion of a run the catalyst was deactivated by the addition of 2 g of solid sodium bicarbonate. The volatile material was stripped at 115 °C (2 Torr) with the volatiles being collected in two tared traps chilled by crushed dry ice. Material balances were generally good to ±0.5%. The volatile fraction was split into two portions, one of which was analyzed for water,[14] the other of which was dried over sodium sulfate and subjected to GLC analysis (Wilkens-Aerograph A-350-B_1, 6 ft × ¼ in. 10% Carbowax 20M on Chromosorb W at 138 °C, 60 ml/min He flow). Relative sensitivity factors, by weight, catharometer detector, were: (component, relative sensitivity, retention time relative to air) THF, 1.22, 1 min; dioxane, 1.00, 1.2; ECH, 1.03, 2.1; CMMD,[4b,c] 0.90, 3.4 and 4.3; CMD, 0.83, 10.5.

The adduct was allowed to stand, molten, for several hours and the clear melt was decanted into bottles for storage. Some of the samples were analyzed for water,[13] hydroxyl number,[14] and hydrolyzable chlorine.[15] Several samples were subjected to gel permeation chromatography to determine the molecular weight distribution[16] (10^5, 10^4, 3000, 10^3, U-Styragel, dioxane, ambient temperature).

Preparation of *cis*- and *trans*-4-Chloromethyl-2-methyl-1,3-dioxolane[4] (CMMD). To a flask containing 22.1 g (0.2 mol) of 3-chloro-1,2-propanediol and 0.2 g of methanesulfonic acid was added, with stirring, 19.2 g (0.2 mol) of isobutyl vinyl ether. The reaction mixture was neutralized with sodium bicarbonate and distilled through a 1-m column containing a Nichrome spiral. The fraction boiling at 147–151.5 °C was collected. Yield 20.2 g, 74%. A GLC analysis showed the presence of two components. The NMR spectrum[17] showed a pair of doublets at 1.38 ppm, complex multiplets over the range 4.5–2.4 ppm, and a multiplet at 5.1 ppm relative to TMS. Integral ratios for these signals were 3:5:1, respectively. The mass spectrum[18] showed a parent peak of 136 (and 138) and a base peak of 121. The mass and NMR spectra were identical with those of material isolated from the appropriate GLC peaks of an actual run. The product was also prepared using boron trifluoride etherate as the catalyst.

Preparation of 2-Chloromethyl-1,4-dioxane[5] (CMD). To a flask containing 310 g (5 mol) of ethylene glycol and 0.6 g of boron trifluoride etherate was added, with stirring, 462.7 g (5 mol) of epichlorohydrin, during a 1-h period with the temperature maintained by water cooling at 60–65 °C. After stirring for two additional hours at 60–65 °C, 1 g of sodium bicarbonate was added to neutralize the catalyst. Distillation resulted in 105 g of crude 1-chloro-3-(2-hydroxyethoxy)-2-propanol, distilling at 123–135 °C (2 Torr).

Sulfuric acid (2 g) and 55 g of this fraction were pyrolyzed by heating to 210 °C. Product (40.5 g) was collected at a vapor temperature of 145–155 °C. Upon redistillation at atmospheric pressure, a 36.5-g fraction, boiling at 175–176 °C, was obtained which was identified by GLC, NMR, and mass spectrometry as 2-chloromethyl-1,4-dioxane of nearly 100% purity.

The NMR spectrum[17] consisted of a complex multiplet centered at 3.73 ppm. The mass spectrum showed a parent peak at 136, an M + 2 peak ⅓ the size of M, and strong peaks at 93 and 87. The mass spectrum was identical with that from material obtained from GLC peak 5 from volatiles obtained in a run.

Reaction of α-Hydro-ω-hydroxypoly(oxy-1,2-ethanediyl) (I) with 3-Chloro-1,2-propanediol. In companion experiments, I (mol wt 1480 and 588) were treated with 0.2% BF_3 etherate and 3-chloro-1,2-propanediol under run conditions at 80 °C. The reaction mixtures were stripped, the material in the traps was diluted with freshly distilled THF, and a portion of the material was dried and subjected to GLC analysis. In both cases the *cis*- and *trans*-CMMD peaks were observed but the other components were absent.

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(17) Performed by William Floutz, of Analytical Research Department, using a Varian T-60 NMR spectrometer.
(18) Obtained by Joel Sibul, of Analytical Research Department, using a Bendix Time-Of-Flight spectrometer.

Interpenetrating Polymer Networks Based on SBR/PS.
1. Control of Morphology by Level of Cross-Linking

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ABSTRACT: Interpenetrating polymer network materials (IPN's) and semi-IPN's have been synthesized from styrene–butadiene copolymers (SBR) as polymer I and polystyrene (PS) as polymer II. Synthetic details, such as the degree of cross-linking of each component, composition, and chemical compatibility, have been varied and their effect on the two-phase morphology has been examined by electron microscopy. The cross-link levels of both polymer I and polymer II were varied from zero to moderately high values. The polymer synthesized first forms the more continuous phase and tends to control the morphology. The second polymer forms a cellular structure whose size is determined principally by the degree of cross-linking of polymer I, with an increase in cross-linking producing a finer structure.

Ideally, interpenetrating polymer networks (IPN's) are a special type of polymer mixture parallel to blends, blocks, and grafts. They consist of two polymer networks synthesized sequentially within each other.[1,2] In real materials, the method of synthesis accidently introduces some grafting, so that the IPN's satisfy all of the generic requirements designated for graft copolymers. When the cross-links outnumber the grafts, however, new morphologies and properties are developed yielding the special characteristics of double networks.

For IPN's the degree of interpenetration depends upon the compatibility among components. In the case of high compatibility, the networks can be visualized as being interpenetrating and continuous throughout the entire macroscopic sample. However, if the components consist of chemically distinct polymers, incompatibility and some degree of phase separation occurs.[2–10] Even under these conditions, the components are intimately mixed, and the phase domain dimensions are on the order of hundreds of Ångströms. If one polymer is elastomeric and the other plastic at use temperature in a two-component system, the IPN behaves synergistically, and either reinforced rubbers or impact resistant plastics result, depending upon which phase predominates.[7,10]

In this and the following paper, the synthesis, morphology, and mechanical behavior of IPN's based on styrene–butadiene rubber (SBR) and polystyrene (PS) will be explored. The principal chemical variables include a systematic variation of the cross-link levels of both polymer I and polymer II from zero to medium levels, and alteration of the polymer I/polymer II ratio. This paper includes synthesis, morphology, and phase domain size, and the following paper centers on dynamic mechanical spectroscopy and general mechanical properties.

The major questions which will be emphasized and require understanding in this study are: (1) How do the synthesis variables of cross-linking, composition, and chemical compatibility affect morphology? (2) How does morphology affect mechanical properties? (3) What are the mechanisms that promote toughening?

Nomenclature

In general, when polymer II is synthesized in the intimate presence of polymer I, the material is known generically as a graft polymer, regardless of the extent of actual chemical grafting.[11–14] Introduction of deliberate cross-linking in both polymers leads to the IPN's. When polymer I is cross-linked and polymer II is not cross-linked, the products will be designated as semi-IPN's of the first kind (semi-1). When polymer I is not cross-linked but polymer II is cross-linked, the products will be designated as semi-IPN's of the second kind (semi-2). In the following, the terms "IPN's" and "full IPN's" are used interchangeably, the latter when greater clarity is required. Polymer nomenclature for graft copolymers and IPN's is developed elsewhere.[15,16]

Experimental Section

(A) Materials. SBR has been selected as the component for the rubber phase, and PS has been chosen for the plastic phase. The SBR polymers were supplied by the General Tire and Rubber Co., Akron, Ohio and Cellomer Associates, Inc., Webster, N.Y. Styrene monomer was obtained from Fisher Chemical Co., Philadelphia, Pa.

(B) Synthesis and Composition. The IPN's and semi-IPN's were synthesized by thermal polymerization techniques. The rubber phase for the semi-IPN's of the first kind and for the full IPN's was prepared by dissolving the SBR in benzene, adding the appropriate amount of dicumyl peroxide (Dicup) for cross-linking, and then evaporating the solvent. The SBR was then cured in a compression molding operation at a temperature of 325 °F and at a pressure of 40–50 psi for 45 min.

In order to form the plastic phase of the semi-IPN's of the first kind and the full IPN's, styrene monomer solutions were prepared containing 0.4% w/v dicumyl peroxide and the appropriate amount of