Simultaneous Interpenetrating Networks Based on Castor Oil Elastomers and Polystyrene. 2. Synthesis and Systems Characteristics

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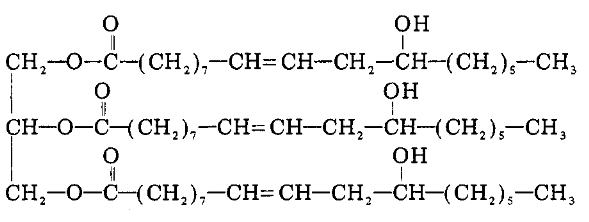
ABSTRACT: The synthesis of simultaneous interpenetrating networks (SIN's) based on elastomeric polymers derived from castor oil and cross-linked polystyrene was studied. The elastomers employed included the cross-linked polyester of castor oil and sebacic acid, the cross-linked polyurethane with 2,4-tolylene diisocyanate, and the cross-linked poly(ester–urethane) from castor oil, sebacic acid, and 2,4-tolylene diisocyanate. The polystyrene phase was cross-linked with 1% divinylbenzene (55% solution), and 0.4% benzoyl peroxide was used as the initiator for the styrene polymerization. This paper describes the synthesis, kinetics, chemical characteristics of the systems involved, and effect of each on the resulting two-phase morphology. Solubility and kinetic considerations showed that either a monomer or prepolymer mixture can be employed for the synthesis of polyurethane SIN's, while a polyester prepolymer was required for the polyester SIN's. Two main compositions having 10 and 40% of the elastomer component were studied. Such materials behaved as tough plastics and reinforced elastomers, respectively. The morphology of the SIN's was found to be sensitive to synthetic details, such as the reaction time with stirring and time of pouring into the mold, after which the reaction was continued without stirring. A definite "window" was shown to exist, controlled by the time required for phase inversion on one side and the time to reach gelation on the other. Morphology studies throughout the course of the polymerization revealed that with proper stirring a phase inversion occurs for compositions up to about 15% castor oil elastomer content. The polystyrene phase cannot be made the continuous phase by mechanical stirring above 15% castor oil elastomer content. A detailed description is given of the morphological stages of the reaction mixture during polymerization, as well as a discussion of the roles of the relative polymerization rates, and polymer I/polymer II compatibility throughout the synthetic process.

Polymer blends as a class of materials encompass many different products resulting from the combination of two or more polymer components. Usually the components differ chemically, and thermodynamic incompatibility due to the low entropy of mixing of long chains causes some degree of phase separation.[1-10] Phase domain size,[11,12] amount of grafting between the components,[13-15] the presence or absence of cross-linking,[16,17] as well as the homopolymer properties constitute very important variables in any real combination. If one polymer is elastomeric and the other polymer is plastic at use temperature, the polyblend tends to behave either as a high impact plastic or as a reinforced elastomer, depending upon which phase predominates. Mechanical blends,[18,19] graft copolymers,[20,21] and block copolymers[22,23] result in thermoplastic polyblends, while the simplest case of thermoset polyblends is the materials known as AB cross-linked copolymers.[24-26]

Materials known as interpenetrating polymer networks, IPN's, contain two or more polymers, each in network form.[27-33] A practical restriction requires that at least one of the polymer networks has been formed (i.e., polymerized or cross-linked) in the immediate presence of the other. Two major types of IPN synthesis have been explored. The first type, termed sequential IPN's, involves the preparation of a cross-linked polymer I, a subsequent swelling in network II monomer components, and polymerization of the monomer II in situ.[27,30,34,35]

The second type of synthesis yields materials known as simultaneous interpenetrating networks (SIN's) and involves the mixing of all components in an early stage, followed by the formation of both networks via independent reactions proceeding in the same container[36,37]. One network can be formed by a chain growth mechanism and the other by a step growth mechanism, which keeps the possibilities of grafting between the homopolymer networks at a minimum. Thus, for example, epoxy/acrylates,[38] polyurethane/polystyrene,[39] polyurethane/polyacrylate,[40] and polyester/polystyrene[41] SIN systems have been studied.[42,43]

Recently, the use of renewable resources has become of increasing interest because of their potential to substitute for petrochemical derivatives.[44-46] Among all the vegetable oils, castor oil has very special characteristics that have made it one of the most important commercial oils. Extracted from the beans of the plant *Ricinus communis* that grows throughout much of the tropical world, it is one of the few naturally occurring triglycerides that approaches being a pure compound, and it is the only major oil composed essentially of the triglycerides of a hydroxy acid, ricinoleic acid, shown below:



$$\begin{array}{l} \mathrm{CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}(CH_2)_7{-}CH{=}CH{-}CH_2{-}\overset{\overset{OH}{|}}{C}H{-}(CH_2)_5{-}CH_3} \\ \mathrm{|} \\ \mathrm{CH{-}O{-}\overset{\overset{O}{\|}}{C}{-}(CH_2)_7{-}CH{=}CH{-}CH_2{-}\overset{\overset{OH}{|}}{C}H{-}(CH_2)_5{-}CH_3} \\ \mathrm{|} \\ \mathrm{CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}(CH_2)_7{-}CH{=}CH{-}CH_2{-}\overset{\overset{OH}{|}}{C}H{-}(CH_2)_5{-}CH_3} \end{array}$$

It is worth emphasizing here that sebacic acid is commercially produced from castor oil, and, therefore, the polyester formed by reacting these two components forms an entirely castor oil based elastomer.

Experimental procedures for the preparation of polyurethane elastomers from several polyols derived from castor oil have been described by Patton et al.[47] The combination of diisocyanates with linear prepolymers having terminal hydroxyl groups to obtain linear polymers

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Table I
Description of Raw Materials and Technical Data

material	abbreviation used	source	technical data and notes
styrene	S	Fisher Scientific Co.	purity 98–99%; density at 25 °C, 0.909; stabilized with *p-tert*-butyl catechol
divinylbenzene	DVB	K&K Lab., Inc.	liquid; technical grade; 55% solution isomers
benzoyl peroxide	BP	K&K Lab., Inc.	used as received
castor oil	CO	NL Industries, Inc.	71001 DB grade; density at 25 °C, 0.957 g/cm^3; M_w = 925.8; hydroxyl functionality, 2.7; moisture < 0.4%
sebacic acid	SA	Eastman Kodak Co.	reagent grade; M_w = 202.25; mp 133–135 °C; functionality, 2
sebacyl chloride	SC	Eastman Kodak Co.	reagent grade; density at 25 °C, 1.1212; functionality, 2; mp −2 °C; bp 220 °C
poly(sebacic anhydride)	PSA	Anhydrides and Chem. Inc.	% anhydride-34.0 min; % free acid-5% max; mp −72–82 °C; sp. gr, 1.0–1.1
2,4-tolylene diisocyanate	TDI	Haven Industries Inc.	reagent grade; density at 25 °C; M_w = 174; functionality, 2.0
catalyst T-9	SOCT	M T Chemicals Inc.	short-chain stannous-type catalyst
catalyst T-6	SOLT	M T Chemicals Inc.	long-chain stannous-type catalyst
catalyst fascat 401	DBTO	M T Chemicals Inc.	dibutyltin oxide

results in polyurethanes such as the so-called segmented elastomers.[1] On the other hand, network polyurethanes are obtained either by reaction of a diisocyanate with a glycol, in the presence of a polyol as a cross-linker, or with a preformed step growth linear polymer containing hydroxyl end groups. The latter synthesis uses branching and cross-linking via amine addition or via urethane–allophanate formation at high temperature.[48]

Earlier work in this laboratory involved the use of castor oil polyurethanes in the synthesis of sequential IPN's[49–51] and resulted in elastomeric, leathery, or plastic materials with improved properties. The purpose of this paper will be to describe the synthesis and kinetics of SIN's based on castor oil elastomers and polystyrene, as well as the role of processing on the morphology of the final polyblend. This paper will be followed by a detailed study of morphology,[52] mechanical behavior,[53] and general properties.[54]

Experimental Section

Materials. Simultaneous interpenetrating networks based on three different castor oil elastomers and polystyrene networks were synthesized; a description of the raw materials employed is given in Table I. The styrene monomer was washed prior to use with 10 wt % NaOH aqueous solution to remove the inhibitor, washed with deionized water, dried using anhydrous calcium sulfate (Drierite), and finally distilled at 40–50 °C under 2.6–4.0 kPa of pressure. Divinylbenzene (DVB), a cross-linker for styrene, was technical grade containing 55% of para and meta isomers. Styrene–DVB mixtures were combined by volume by adding 1 mL of DVB technical solution to 99 mL of styrene monomer. The toluene, having 0.02% water content, was further dried by calcium sulfate addition before use.

Instrumental Techniques and Measurements. A. Swelling Tests. Several homopolymer specimens of each network, measuring about 0.5 × 0.5 × 1.0 cm, were weighed then swollen in several solvents for 1 week at room temperature according to a technique described elsewhere[55] and reweighed to determine the quantity of solvent imbibed.

B. Polyurethane Gel Times. Ten samples were tested in tightly capped vials. The separate reactant components were weighed at room temperature and then placed in a preheated oven at the test temperature for at least 12 h until thermal equilibrium was reached. Reactant weights were quickly checked and the components mixed, stirred, and placed in a silicone oil bath at the test temperature. The gel point was judged to occur at the point at which the system lost apparent fluidity. This point was rather sharp and the gelation process was complete in about 1–5 min, depending on solvent concentration.

C. Polyesterification Kinetics. Polyesterification reactions were followed experimentally by titrating the unreacted carboxyl groups with a standard solution.[56] A 500-mL resin bottle equipped with a nitrogen inlet, thermometer (0.02 °C divisions), high-torque stirrer, distilling Barret trap, and Friedrichs condenser was chosen as the polymerization reactor system. The reactions were carried out under a N_2 flow of 40 cm^3/min. The temperature was maintained within ±2 °C by using a Thermocap Relay controller. Conversions near the gel point were determined by transferring 50 g of the mixture to a filter flask, and continuing the reaction at 175 °C under a reduced pressure of 10–100 Pa. When the gel point was reached, the sample was quickly cooled, and the average of three acid value determinations was taken.

D. Electron Microscopy. Sample preparation was based on Kato's osmium tetroxide staining technique.[57] Samples of 0.2 × 0.2 mm cross-section and lengths ranging from 0.2 to 10 mm were exposed to osmium tetroxide vapor at room temperature for 1 week in order to selectively stain the double bond of the castor oil phase. Sections of the stained specimens were imbedded in an epoxy resin, trimmed to a truncated pyramid shape, and microtomed in a Porter Blum MT-2 ultramicrotome using a diamond knife.[58] Ultrathin sectioning at room temperature to thickness of 600 to 800 Å yielded satisfactory results. Transmission electron micrographs were taken employing a Philips 300 electron microscope.

Synthesis. Three groups of materials were obtained by changing the nature of the castor oil based elastomer. Step growth polymerization using the hydroxyl groups in the oil yielded a polyester, a polyurethane, and a mixed polyester–urethane elastomer. Since reactivities of the different functional groups involved in the reaction make the synthesis procedure different, each of these syntheses will be described briefly under a separate heading.

Homopolymer Networks. A. Castor Oil Polyester Networks (COPEN). Polyester networks (COPEN) were obtained by reacting castor oil with sebacic acid under appropriate conditions to give reasonable gel times. Polyester elastomers having COOH/OH ratios of 1.0, 0.9, and 0.8 were obtained by varying the reaction proportions. Several different soluble-type tin-based catalysts were studied in a preliminary series of experiments. A catalyst concentration of 0.1 wt % of stannous ion based on total charge was used in the castor oil–sebacic acid and castor oil–PSA reactions. These reactions were carried out at temperatures ranging from 180–200 °C in the 500-mL reactor described above. Close to the gel point, the reactant mixture was cooled down to 170 °C, degassified by applying a vacuum, and poured into Teflon-lined molds. Table II gives the composition and properties of the polyester prepolymers at this point. The reaction was completed at 180 °C in an oven filled with N_2 over a 24-h period. A vacuum was applied during the next 24 h to force the reaction toward the polyester formation by increasing the rate of water removal. Polyester networks were also obtained by reacting castor oil and sebacyl chloride at temperatures between 0 and 40 °C. A typical synthesis involved the mixing of the comonomers, stirring

Table II

Composition, Characteristics, and Curing Conditions of Castor Oil Prepolymers (Base: 100 g of Final Elastomer)

Polyester

	prepolymer					curing	
designation	castor oil	sebacic acid	COOH/OH	conversion p	acid value	conversion at gel point	conditions
COPEP1	80.48	23.73	1.0	0.740	33.0	0.760	T 180–200 °C
COPEP2	82.09	21.79	0.9	0.785	25.2	0.807	P 3.0 kPa
COPEP3	83.76	19.76	0.8	0.840	17.1	0.857	t 48 h

Poly(ester-urethane)

	prepolymer					curing		
designation	castor oil	sebacic acid	COOH/OH	conversion	acid value	curing agent	wt	conditions
COPEP4	80.07	14.17	0.6	0.988	1.5	TDI	8.28	T 80–130 °C P 100 kPa t 3–24 h

Polyurethane

	prepolymer				curing		
designation	castor oil	TDI	NCO/OH	equiv wt/NCO	curing agent	wt added	conditions
COPUP1	36.26	20.23	2.2	445.3	castor oil	43.5	T 80–130 °C P 100 kPa t 3–24 h

for 1–5 min, degassing by vacuum, and pouring into molds. After gelation, the sample was removed from the molds and cured by applying either vacuum or dry nitrogen. The reaction was usually complete within 2–3 h.

Poly(sebacic anhydride) (PSA) was also employed for a few experiments. The reaction conditions were essentially identical to those described for sebacic acid above.

B. Castor Oil Polyurethane Networks (COPUN). Synthesis of urethane elastomers was carried out by reacting equivalent amounts of castor oil and 2,4-tolylene diisocyanate (TDI) to give a NCO/OH ratio of unity. Bubble-free elastomers were obtained either by using the prepolymerization step used by Yenwo et al.[49] in the synthesis of sequential castor oil polyurethane–polystyrene IPN's or by adding 20% vol of dried toluene to the reaction mixture. In brief, an isocyanate chain ended prepolymer was first prepared by adding 1 equiv of castor oil to 2.2 equiv of 2,4-TDI, with stirring, at a temperature which was always kept below 70 °C. After being stirred for 2 h, the prepolymer was degassed until a clear viscous liquid was formed, COPUP1. Fully reacted samples were then prepared by adding castor oil to the mixture and mixing for 10 min with a high torque stirrer and then degassing and pouring the mixture into the molds. Samples were cured at 80 °C for 24 h followed by 2 h at 130 °C. Table II shows the composition and characteristics of the prepolymer as well as the curing conditions.

C. Castor Oil Poly(ester–urethane) Networks (COPEUN). The third type of castor oil elastomer was synthesized by a combination of the two methods described above. A polyester prepolymer was prepared under conditions similar to those described above. However, less sebacic acid (COOH/OH = 0.6) than the minimum amount required for network formation (COOH/OH = 0.64) was charged and reacted almost completely.

Cross-linking of this prepolymer, designated COPEP4, was carried out by first adding 20% of the dried toluene followed by addition of 2,4-TDI under stirring at room temperature. The toluene provided convenient means of handling the elastomers polymerized under conditions similar to those employed in SIN formation. Curing was done at 80 °C for 24 h and 100 °C for 22 h to remove the toluene and 2 h at 130 °C. Table II gives weight proportions used in the synthesis of 100 g of each elastomer.

In some of the materials studied, the final postcuring step was omitted, and hence the castor oil polymer was linear. This is indicated by omitting the "N" for network in the designation.

D. Polystyrene Networks (PSN). Syntheses of polystyrene networks (PSN) were carried out by adding, proportionally, 99 mL of freshly distilled styrene, 1.0 mL of DVB, and 0.4 g of benzoyl peroxide, followed by polymerization at 80 °C for 24 h and 100 °C for 12 h in closed glass molds.

SIN Synthesis. Syntheses of SIN's were carried out by charging the proper amount of the selected castor oil prepolymer into the 500-mL reactor, followed by the addition of the styrene mixture. After stirring and purging with nitrogen for 5–10 min, the curing agent for the elastomer prepolymer was added. All SIN formations gave slightly yellowish but clear solutions. The temperature was raised to 80 °C and polymerization carried out under continued stirring with a nitrogen atmosphere. Pouring the mixture into preheated molds was done after about 30 min for the 40% compositions and from 80 to 120 min for the compositions having 10% or less elastomer content. All samples were polymerized at 80 °C for 24 h and at 100 °C for 12 h. Final sample dimensions were 18 × 18 cm and up to 0.8 cm thick.

Results

Solubility and Swelling. The compatibility of the elastomer network and plastic network prepolymer components during the reaction was studied qualitatively by observing mutual solubility at 80 °C. The onset of cloudiness was judged as the point of phase separation for the components in question.

Several results were found: a. Sebacic acid, with limited solubility in the styrene mixture and castor oil, was found to be solubilized satisfactorily in the polyester prepolymer form. b. All castor oil–polyester elastomers retain clarity and are presumed compatible with the styrene mixture, regardless of molecular weight of the former. This means that all the elastomer networks can be polymerized and gelled in a styrene-swollen state without undergoing phase separation. c. Although styrene monomer is compatible with castor oil (i.e., gives clear solutions), polystyrene is not compatible and attempts to prepare such a solution (CO–PS) always underwent phase separation. Under polymerization conditions, the polystyrene chains precipitated from the styrene–castor oil solution.

Swelling characterization data for the three elastomer networks is presented in Figure 1. The solubility parameter of all the elastomer networks was found to be about 9.3 $(\mathrm{cal/cm})^{1/2}$. This result, identical to the value for styrene monomer, explains the compatibility described above during the elastomer network formation. However,

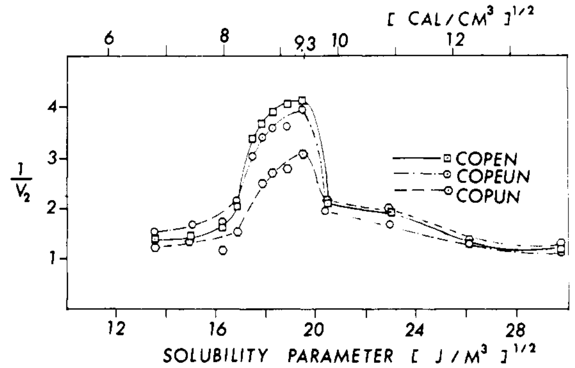

Figure 1. Solubility parameter determination for castor oil based elastomers.

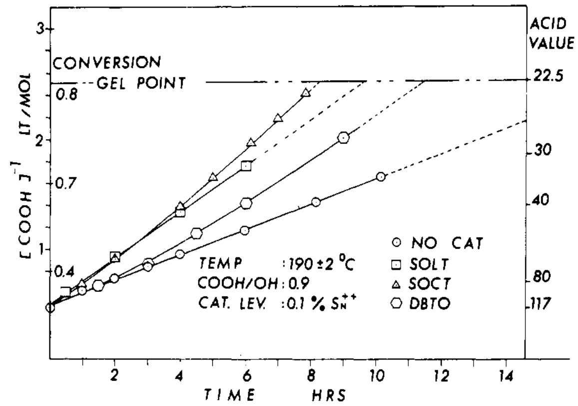

Figure 2. Kinetic data for the castor oil–sebacic acid polyesterification reaction during catalyst evaluation at 190 °C.

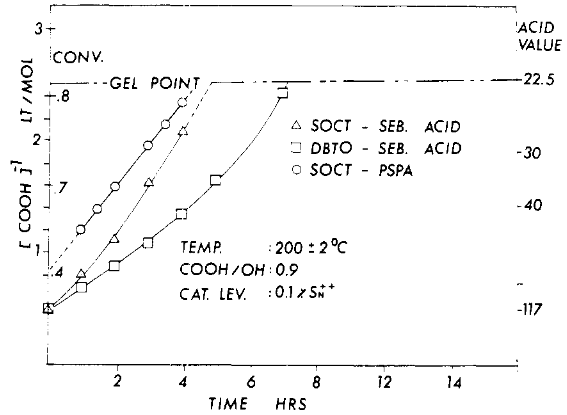

Figure 3. Kinetic data for the castor oil polyesterification reaction during catalyst evaluation at 200 °C.

it is thought that the method employed does not resolve the small solubility parameter differences existing among the three elastomer networks studied.

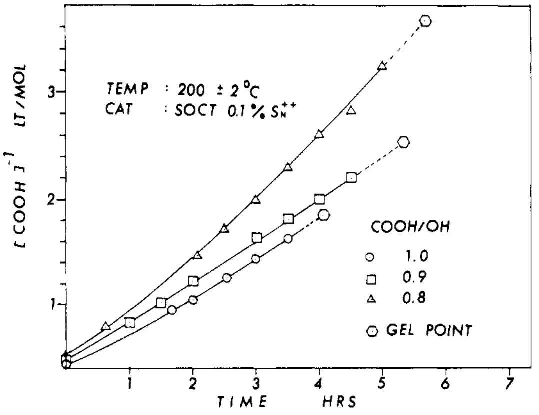

Figure 4. Kinetic data for the castor oil–sebacic acid polyesterification reaction at 200 °C using 0.1% Sn^{2+} SOCT catalyst.

Table III
Gel Point Determinations for Mixtures of Sebacic Acid and Castor Oil

prepolymer designation	composition ratio COOH/OH	extent of reaction at gel point (P_c)		
		obsd[a]	calcd from C[b]	calcd from FS[c]
COPEP1	1.0	0.760	0.870	0.767
COPEP2	0.9	0.807	0.911	0.808
COPEP3	0.8	0.857	0.963	0.858

[a] A molecular weight of 925.8 and 2.7 OH/molecule was assumed for the oil. [b] Calcd from Carothers eq 1. [c] Calcd from Flory–Stockmayer eq 2.

Kinetics. A. Reactivity and Gelation Behavior of Castor Oil Based Polyesters. The esterification reaction of castor oil with sebacic acid proceeds very slowly at low temperatures, and, therefore, reaction temperatures below 180 °C were not practical. Since acid catalysts may dehydrate the oil, organometallic catalysts were tested at a fixed concentration of 0.1 wt % active metal ion based on total charge. The reaction was followed by titrating the free acid groups with a standard alcoholic potassium hydroxide solution.[56] Figure 2 depicts the performance of several catalysts at 190 °C showing that the use of SOCT catalyst (see Table I for catalyst description) considerably reduces the time required for gelation, from 18 h compared to 8 h for the catalyzed reaction.

SOCT and DBTO (see Table I) were chosen to be tested at 200 °C because they also gave satisfactory results such as good color and clear prepolymers. Figure 3 compares the performance of SOCT and DBTO catalysts at 200 °C. Both catalysts were considered satisfactory but SOCT gave the better overall performance. All prepolymers were clear viscous liquids having color characteristics only slightly different from those of the oil.

Figure 3 also illustrates kinetic differences if poly(sebacic anhydride) is used. As expected, shorter reaction times to gelation were obtained, but such differences between PS and sebacic acid tended to be quite small at high conversions. Under experimental conditions, the use of PSA shortened gel times approximately 30 min. Thus SOCT and sebacic acid were used in the main synthesis of the polyester prepolymers described in Table II.

Figure 4 shows kinetic data for the castor oil–sebacic acid system as a function of the concentration ratio COOH/OH in the mixture and indicates the time of gelation. For COPEN, COPEUN, and COPUN reacting mixtures, the Carothers equation[56] for predicting the extent of reaction at the gel point (P_c) can be written as:

$$P_c = 0.5 + \frac{1}{rf_0} \tag{1}$$

while the Flory–Stockmayer equation[56,57] can be written as:

$$P_c = \frac{1}{r(f_0 - 1)} \tag{2}$$

where f_0 is the hydroxyl functionality of the oil and r is the total composition ratio (COOH + NCO)/OH. Table III compares the experimental and predicted extents of reaction at the gel points for the polyester reaction mixtures. The experimental data agree remarkably well

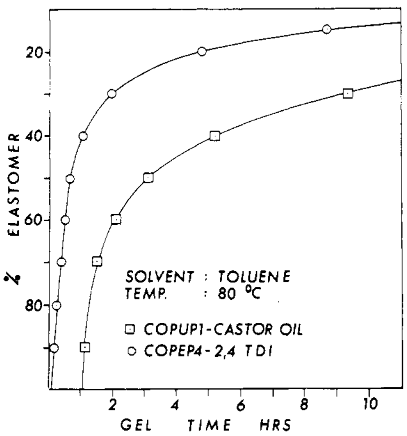

Figure 5. Dilution effect on the gel point of castor oil prepolymers.

Table IV
Effect of Elastomer Concentration on the Gel Point of the Styrene Network

wt % of the styrene mixture[a]	wt % of the 2nd component	gel time, min
100	0	110
95	5 (COPEP1)	120
90	10 (COPEP1)	140
80	20 (COPEP1)	not observed

[a] Polymerization at 80 °C, with 1% DVB.

with predictions using the Flory–Stockmayer equation,[59] based on the statistical approach. The Carothers equation[59] predicts a higher conversion at the gel point, because it assumes that gelation takes place when the number average molecular weight becomes infinite.

Equation 2 can be rearranged so that P_c/f_0 appears in place of 0.5 in eq 1. Since P_c has a maximum value of 1, and f_0 has a value of 2.7, a maximum value of 0.37 for the constant is obtained. Table III shows the Carothers value to be high by about 0.11, in confirmation of these calculations.

B. Reactivity and Gelation Behavior of Castor Oil Polyurethanes. Gelation of the COPUP1–castor oil reaction was observed by measuring the gel times as a function of total elastomer content in a solution of the reactants in dried toluene at 80 °C. Results are shown in Figure 5. Gelation occurs between 60 and 80 min for samples having above 50% elastomer content, while the time required to gel samples below 30% elastomer content increases significantly. Gelation was observed to occur up to 90% toluene content within a period of 10 days. The gelation time was always sharp although the stiffness of the gel formed depends on the elastomer concentration. All gels were clear, indicating retention of a single phase.

C. Reactivity and Gelation Behavior of Castor Oil Poly(ester–urethane). Times to gel as a function of the poly(ester–urethane) elastomer content in toluene solution are also plotted in Figure 5. It is observed that since COPEP4 starts very close to gelation (COOH/OH = 0.6), gel times are considerably shorter than those for the COPUP1–castor oil mixture. Samples containing above 20% of the elastomer gelled with an 8-h period, yielding single-phased, clear gels.

D. Reactivity and Gelation Behavior of Polystyrene Cross-Linked with Divinylbenzene. The gel point of the styrene mixture at 80 °C was found to be about 110 to 115 min. Gel time increases as shown in Table IV in the presence of castor oil or castor oil prepolymers. A solution of castor oil–sebacic acid polyester prepolymer in the polymerizing styrene mixture undergoes phase separation at around 25 to 35 min. At 20% castor oil prepolymer content, however, gelation was not observed. As explained below, this material fails to undergo phase inversion. All gels formed were opaque revealing the coexistence of two separate phases.

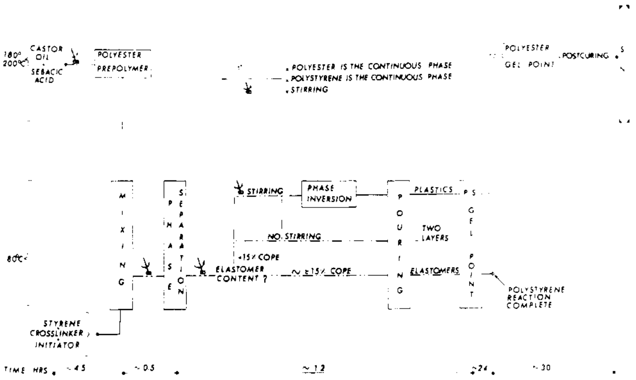

Figure 6. A process scheme for the synthesis of castor oil polyester SIN's.

Morphology Changes during the Synthesis of SIN's. During the chemical process by which a solution of comonomers is transformed into a SIN, several morphological changes occur. The path of morphological changes depends on overall composition, solubility relationships, reaction rates, and the rate of stirring, if any. As an example, the morphological paths of the COPEN/PSN materials will be described below employing the synthetic scheme shown in Figure 6.

Castor oil and sebacic acid are reacted at 180–200 °C until the mixture approaches gelation, so a branched prepolymer having an equal number of both functional groups (COPEP1) is obtained (Figure 6, upper left). Due to the high temperatures required for polyester formation, the reaction is readily stopped by cooling the prepolymer to 80 °C. The styrene comonomer mixture is prepared at room temperature and charged to the reactor containing the polyester prepolymer, where mixing takes place (Figure 6, lower left). This yields a mutual solution of all components required for the formation of both networks. The temperature is then raised to 80 °C in order to initiate the styrene polymerization. (The polyester reaction rate is nil at this temperature.) In polymerizing the styrene component within the polyester prepolymer mixture, the first amount of polystyrene produced early in the reaction remains dissolved until some critical concentration is reached, followed by phase separation.

The solution is transformed to an oil-in-oil emulsion in which a polystyrene solution forms the disperse phase and the elastomer polyester component solution the continuous phase. The point of phase separation is observed experimentally by the onset of turbidity, due to the Tyndall effect. The conversion required for phase separation to occur depends basically on the solubility of the polystyrene chains in the elastomer solution, which in turn is governed by the elastomer concentration and compatibility of the two polymers.

As polymerization proceeds, the total volume of polystyrene polymer particles increases rapidly at the expense of the styrene monomer from the solution. What happens next depends on several factors, mainly composition and stirring. It was found that for SIN formulations having an elastomer content greater than about 15%, the elastomer material will remain the continuous phase, regardless of the extent of agitation as illustrated in the transmission electron micrographs in Figure 7 for a 20/80

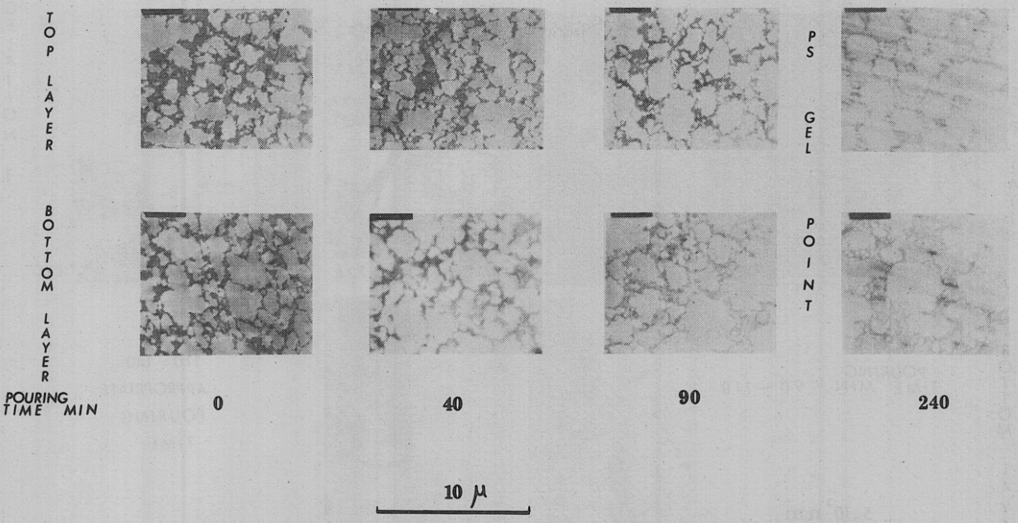

Figure 7. Morphology changes induced by stirring during the synthesis of a 20/80 COPE/PSN SIN.

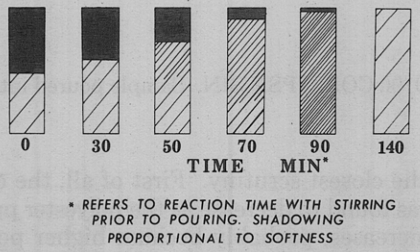

Figure 8. Layering effect during the synthesis of a 10/90 COPEN/PSN SIN.

COPEN/PSN composition.

However, for SIN's having up to 10–15% elastomer content, it was found that stirring induces significant changes in the morphology of the mixture. If stirring is not provided, the polystyrene polymer particles will sink and coalesce giving rise to a two-layered system.

The upper layer possesses more elastomer which forms the continuous phase, and the bottom layer has PS as the continuous phase.

Samples prepared with stirring and poured into test tubes at different times (stopping the stirring) showed the sequence illustrated schematically in Figure 8. The two layers were distinguishable because of dullness and hardness differences. The layering effect observed for short reaction times indicates a gross incompatibility of these materials. For the several reasons noted below, continued stirring promotes mixing on a finer scale in the final product. At a reaction temperature of 80 °C, the volume of the upper layer (elastomer continuous) decreases slowly and finally disappears at about 90 min. Samples of both top and bottom layers were studied by transmission electron microscopy techniques, and micrographs for a 10/90 COPE/PSN are shown in Figures 9–11. Samples up to 90 min exhibit the same morphological pattern shown in Figure 9. At 90 min, and coinciding with observed disappearances of the upper layer (see Figure 8), a phase inversion takes place. Micrographs T2A, T2B, and T2C in Figure 10 were all taken from the top layer and illustrate the process of phase inversion. At T2A the castor oil elastomer (stained dark by the OsO_4) forms the continuous phase. Micrograph T2B shows the polystyrene domain coalescence process by which elastomer domains are generated and a polystyrene continuous phase begins to form, thus illustrating the actual phase inversion point. Micrographs T2C and B2 show that at the end of the phase inversion the top and bottom regions have identical morphologies and the sample attains macroscopic homogeneity.

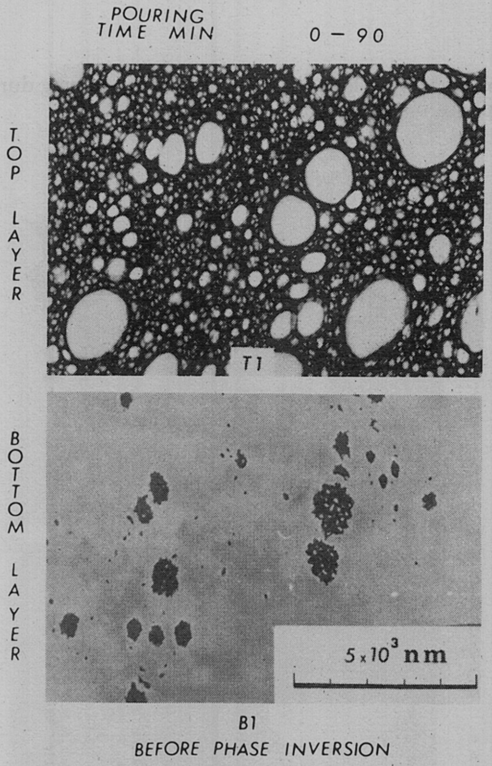

Figure 9. Morphology changes induced by stirring during the synthesis of a 10/90 COPE/PSN SIN. The sample was poured into the mold before phase inversion.

It was observed above that the volume of the polystyrene phase increases at the expense of the styrene monomer. Eventually a point in conversion is reached in which the volume fraction of the polystyrene solution becomes comparable to that of the elastomer phase and, therefore, more likely to become the continuous phase. Indeed, provided that strong agitation is maintained, a phase inversion does occur and the elastomer phase breaks into large particles (2–5 × 10^3 nm) forming the discontinuous phase. Due to the high viscosity of both components, a spontaneous phase inversion fails to occur in the absence of strong mechanical stirring. Indeed, micrograph T2B was taken by stopping the stirring at the critical point. During a short interval following phase inversion, shear action

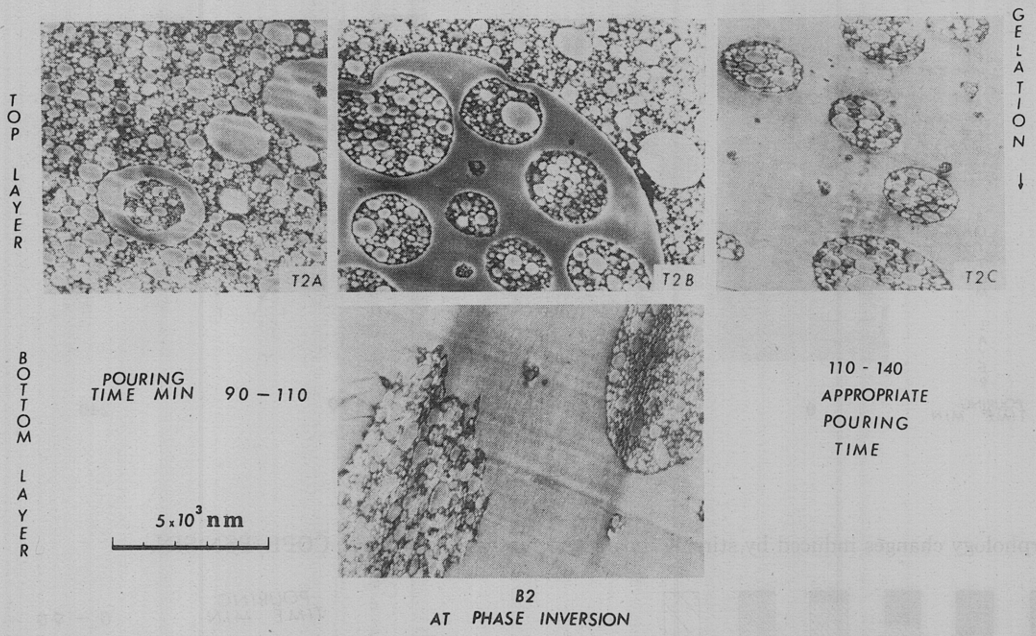

Figure 10. Morphology changes induced by stirring during the synthesis of a 10/90 COPE/PSN SIN. Sample poured into the mold at the phase inversion point.

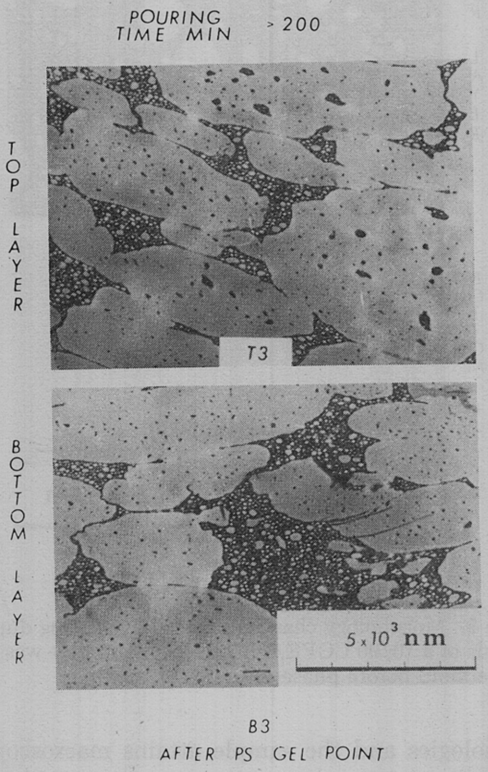

Figure 11. Morphology changes induced by stirring during the synthesis of a 10/90 COPE/PSN SIN. The sample was poured into the mold after the polystyrene gel point.

induced by stirring breaks the large elastomer particles into smaller ones.

In the time interval between phase inversion and gelation of the polystyrene continuous phase, the final morphological features such as size average and size distribution of elastomer domains become fixed. Since these morphological changes affect properties such as modulus and impact resistance, the characteristics of the system at and just after phase inversion and before gelation demand the closest scrutiny. First of all, the open time interval was found to decrease as the polyester prepolymer content increases, probably because higher polystyrene conversions are required for the system to reach suitable phase inversion conditions. Thus, for example, Figure 12 shows that for a 5/95 COPE/PSN, phase inversion occurs earlier than the 10/90 (Figure 10) composition, and the time interval is larger. The end of this interval is determined by the gel time of the PS phase. Thus, for a fixed polyester prepolymer content, the interval length is expected to decrease for higher DVB concentrations.

Since compositions having elastomer contents below 15% are generally formulated to produce high-impact plastics, pouring should be done within the "window" bounded by phase inversion on one side and gelation on the other in order to obtain the desired morphology and concomitant physical and mechanical properties.

If stirring is continued too long, the onset of the gel point is characterized by the appearance of high normal stresses which cause the mixture to climb up the stirrer shaft. Because of the small amount of cross-linker present in both phases when the COPEP1 composition is used, these high normal stresses will decrease and finally disappear if stirring is continued. However, continued stirring of the COPEP1–polystyrene system destroys the correct morphology as micrographs T3 and B3 in Figure 11 show, and poor mechanical properties result.

These high normal stresses at the gel point did not disappear when COPUN or COPEUN elastomers were used. Such observations suggest that differences in behavior may arise due to the presence of some cross-linking in the elastomer particles, which restrict the elastomer particle breakdown process in going from the morphology shown in micrographs T2C and B2 to that shown in T3.

In order to attain good mechanical properties, the synthesis of the SIN must be carried out by pouring the mixture from the reactor to the molds before the gel point, completing the styrene copolymerization at 80 °C, and then raising the reaction temperature to 180–200 °C to complete the polyesterification reaction (center and right-hand side of Figure 6). A postcuring period after polyester network formation was used to assure completion

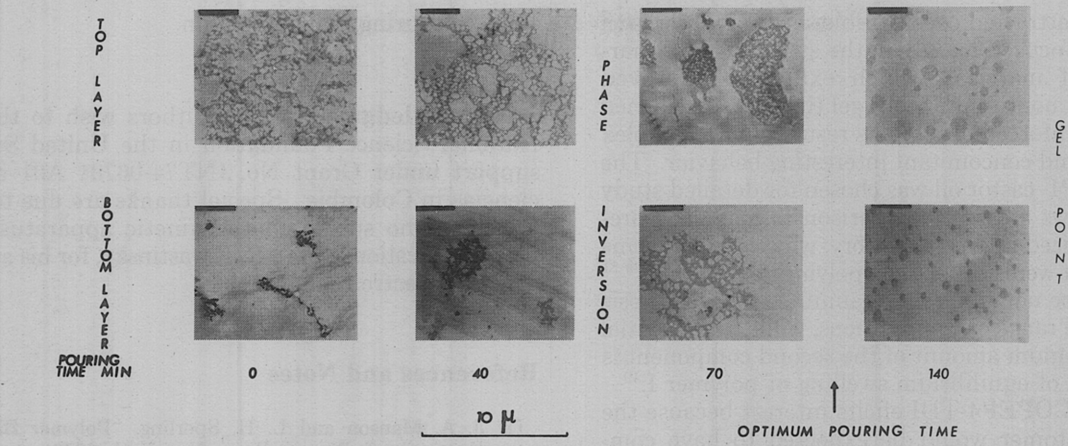

Figure 12. Morphology changes induced by stirring during the synthesis of a 5/95 COPE/PSN SIN.

of the latter reaction, see Figure 6. For the SIN's involving COPEUN and COPUN elastomers, postcuring at 180–200 °C is not required since these networks and cross-linked polystyrene form at comparable rates under the same conditions.

The morphological changes found for the COPEN/PSN system are similar to those observed in the mechanism of domain formation during the synthesis of other rubber modified vinyl polymers.[61-63] Indeed, because of the small amount of cross-linking in both phases and similarities in solubility relationships, the systems COPEP1 polystyrene and poly(butadiene-*g*-styrene) show similar patterns of behavior during polymerization. However, significant differences exist because in the present system grafting is more limited[66] and, therefore, rubber particles are not cross-linked during the styrene polymerization via AB copolymer reactions.[24,64] Another difference arises from the presence of DVB in the polystyrene phase. The morphological paths just described are useful in understanding the effects of several variables on the final morphology. For example, an increase in polystyrene–elastomer compatibility would delay phase separation, which was observed to occur for the 10/90 COPUN/PSN SIN compared to the 10/90 COPEN/PSN SIN.

Discussion

Reactivity of Elastomers. The required set of experimental conditions to obtain polyester and polyurethane elastomers by the reaction of castor oil with sebacic acid and 2,4-toluene diisocyanate was very different. The esterification reaction required temperatures from 180–250 °C, and water given off in the reaction was removed as rapidly as possible. To facilitate water removal at the latter stages of esterification, vacuum was usually applied (10–100 Pa). In general, the reaction time required depended on the reactivity of the mixture, the stoichiometry, the temperature, the pressure, the molecular weight of the resultant polyester, the rapidity with which the water was removed, and the activity of the employed catalyst (if any).

An alternative synthesis route employed sebacyl chloride which reacted very easily with the oil at room temperature to form a soft elastomer. In spite of such desirable high reactivity, the use of sebacyl chloride showed some disadvantages due to side reactions of the HCl evolved with both castor oil and styrene. Network degradation was observed to occur in the first case, especially if the sample was kept at temperatures above 60 °C in closed molds. The presence of a solvent such as toluene and a quick removal of the HCl was found to decrease the rate of network degradation. Hydrolysis of ester groups as well as dehydration of the oil might be possible causes for this phenomenon. In the second case, the presence of a nonpolymerizable liquid fraction obtained by vacuum distillation of the SIN's was detected. Although hydrochloric acid does not interfere with the free-radical polymerization of styrene, it adds by an ionic mechanism to styrene monomer, yielding low molecular weight saturated products such as phenylethyl chloride and oligomers. Thus, although SIN's can be obtained through this route, and indeed yield very interesting products for scientific purposes,[41] the synthesis employing sebacic acid plus tin catalysts proved more practical.

The reaction between a hydroxyl group and an isocyanate group is different from the polyester formation in that it is a double bond addition reaction, which proceeds by an ionic mechanism. The isocyanate group exhibits high reactivity toward a variety of reagents containing an active hydrogen atom such as water, phenols, thiols, amines, amide, and carboxyl groups. At elevated temperatures, side reactions may also lead to additional branching and cross-linking.[48] Side reactions were avoided by the use of reaction temperatures below 120 °C and avoiding either acidic or basic catalysts.

In the poly(ester–urethane) synthesis, an extended chain branched polyester prepolymer having terminal hydroxyl groups is cross-linked by the addition of 2,4-TDI to form urethane linkages. The reactivity of this system in the latter step is, therefore, similar to the polyurethane system.

The Simultaneity Problem. The kinetic and solubility considerations for each component in the castor oil SIN's are very useful in designing synthetic procedures for each SIN system, as well as understanding the different phenomena observed during polymerization of such materials. As far as the polyester elastomers are concerned, it is clear that the use of prepolymers allows the formation of homogeneous comonomer mixtures, i.e., clear solutions. However, the reaction rates for network formation under the same conditions differ significantly, and hence, simultaneity of network formation is not possible.

On the other hand, the range of reaction rates and gel times for the formation of the polyurethanes and poly(ester–urethane) networks is comparable to those of the polystyrene network. In these latter cases, both homopolymer reactions are proceeding simultaneously at 80 °C (i.e., molecular weights of both homopolymers are increasing with time), and provided that an appropriate set of conditions such as composition, temperature, and catalyst concentrations is achieved, both networks can be forced to gel simultaneously. Although this interesting possibility has attracted considerable scientific interest,[27] this work was focused mainly in the synthesis and characterization of materials which exhibited improved properties with nonsimultaneous gel times.[38] Toughened plastics and reinforced elastomers resulted with complex morphologies and concomitant interesting behavior. The system COPUP1–castor oil was chosen for detailed study because it allows a direct comparison to materials previously synthesized in this laboratory, which had the same components but were sequentially polymerized in bulk.[49–51] It also should be noted here that simultaneous synthesis allows an entire range of compositions, while in sequential IPN's the maximum amount of the second component is limited to that of equilibrium swelling of polymer I.[49]

The system COPEP4-TDI elicits interest because the COPEUN elastomer would be expected to have compatibility and glass transition behavior intermediate between the COPEN and COPUN and so offers a convenient reference point in the study of the mechanical properties as a function of temperature.

On Relative Rates of Polymerization. When monomers and/or polymers of a SIN mixture form a true solution, the key aspect to be considered next is the mechanism of network formation. For these systems, properties of the final material will be determined by the morphological state of the mixture at the gel point of the more continuous phase. If one of the networks being formed becomes incompatible with another component, phase separation will occur during polymerization, perhaps before either gel point. In such a case, variables affecting phase inversion (composition, stirring, etc.) should be taken into consideration. For systems containing a continuous and a dispersed phase, the competition of the dispersed phase to reach gel point is not critical since the gel point of the dispersed phase introduces little if any change in the morphology of the final system.

Provided that phase separation does not occur at least up to the gel point of the first network, the chief variable may then be visualized as the competition of both polymers to predominate, that is to reach the gel point.[35] It is thought that the first polymer component to reach gelation will be more continuous in space and thus control the physical and mechanical behavior of the total system out of proportion of its weight fraction.[35,65] Two extremes can thus exist: (a) one network forms at a very fast rate compared to the other, and, in such a case, morphology could be expected to be somewhat similar to that of the bulk sequential IPN's; or (b) both networks reach the gel point at substantially the same time, which should give a maximum of network continuity to both networks constituting the system.

Conclusions

The present synthesis of castor oil based SIN's in bulk involves the transformation of the multimonomer solution into an oil-in-oil emulsion, in which the newly formed polystyrene chains precipitate giving rise to a disperse phase. Stirring is shown to play a very important role in preventing layering of the reaction mixture and inducing phase inversion. With stirring, phase inversion occurs up to about 15% elastomer content. An interval of optimum pouring time exists for samples containing up to 15% elastomer. The time length of this "window" decreases with increasing elastomer concentration. The morphologies described were found to be similar to other graft copolymer systems; however, differences in morphology and behavior are reflected in the usual synthetic paths followed during polymerization.

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(66) Grafting of the castor double bonds is lower than that of polybutadiene for two reasons: (1) lower concentration of double bonds in terms of moles per liter and (2) the OH group α to the double bonds provides a degree of hindrance (58). Also, the molecular weight of the castor oil prepolymer is lower than the polybutadiene.

Hexaarylbenzene Units as Cross-Linking Sites for Polyquinolines

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ABSTRACT: Hexaarylbenzene units were incorporated into a polyquinoline backbone in order to provide a site which could enter into a thermal cross-linking reaction well above the T_g of the parent polyquinoline. The incorporation was accomplished by balancing the appropriate amounts of 1,2-bis(4′-acetyl-4-phenoxyphenyl)-3,4,5,6-tetraphenylbenzene in the place of 4,4′-diacetyldiphenyl ether with 3,3′-dibenzoyl-4,4′-diaminodiphenyl ether in the synthesis of the polyquinoline. The cross-linking reaction occurred rapidly at 400 °C to give insoluble polymers with enhanced mechanical properties.

The high values of T_g often limit the processability of thermally stable polymers.[1] One approach to the solution of this problem is to lower the T_g of the polymer by adding flexible groups such as ethers to allow processing and to convert the polymer to a network structure allowing the polymer to be used well above T_g. A suitable cross-linking agent for this transformation is one that forms thermally stable linkages between the polymer chains.

Recent work in our laboratories has shown that the incorporation of biphenylene into thermally stable polymers[2–5] allows the cross-linking of polymers at 340–380 °C. These cross-linked polymers exhibit higher T_g's and enhanced mechanical properties above T_g. One disadvantage to this curing reaction of biphenylene units is that the temperature range for processing, above the T_g but below the onset of the opening of biphenylene, is narrow. In an attempt to introduce cross-linking groups in a polymer chain that undergo reaction at higher temperatures, the hexaphenylbenzene nucleus was investigated as a reactive group. It had been shown that polyphenylated polyphenylenes cross-linked at elevated temperatures and that radicals were generated at 350 °C.[6]

Because the evolved products from this reaction were benzene and biphenyl, the cross-linking was attributed to the cleavage of phenyl–phenyl bonds, generating a phenyl radical and leaving behind a reactive phenylene radical on the polymer chain. The relative ease of cleavage of the phenyl–phenyl bond as compared to that exhibited for biphenyl, for example, was ascribed to lack of conjugation between phenyls as a result of the crowding of five phenyl groups around a phenylene in the backbone. The placement of six equivalent phenyls on a backbone phe-

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