Polymers with Pendant Isocyanate Groups. I. Dual Synthesis and Properties of Poly(styrene-co-Styryl Isocyanate)

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Synopsis

The copolymer poly(styrene-co-styryl isocyanate) was synthesized directly by radical initiation from two different monomer pairs: styrene–cinnamoyl azide and styrene–styryl isocyanate. The copolymerization parameters $r_1 = 0.93 \pm 0.08$, $r_2 = -0.7 \pm 0.8$ for the first monomer pair and $r_1 = 7.8 \pm 0.6$, $r_2 = 0 \pm 0.3$ for the second pair were determined according to the conventional scheme of copolymerization. The intrinsic viscosities and the thermal behavior of the various copolymers were determined. Further, the chemical reactivity of the pendant isocyanate groups toward alcohol and amines was investigated.

INTRODUCTION

Due to the high reactivity of the isocyanate groups with alcohols, amines, acids, i.e., with compounds containing an active hydrogen, it is of great interest to synthesize polymers laterally substituted with an isocyanate group. By means of the isocyanate groups, these polymers can easily be modified, cross-linked, grafted, etc.

Homopolymers and copolymers of a number of vinyl monomers containing an isocyanate group have been synthesized, and some of them are given in the following survey.

Hart,[1] Schulz and Hartmann,[2] Overberger et al.,[3] and Butler and Monroe[4] have studied the vinyl homopolymerization of vinyl isocyanate, whereas Iwakura et al.[5] and Welzel and Greber[6] have determined the various reactivity ratios for its copolymerization with styrene,[5,6] methyl methacrylate,[6] vinylidene chloride,[5] methyl acrylate,[5] and acrylonitrile.[5] Butler and Monroe[4] prepared copolymers of vinyl isocyanate with styrene, methyl methacrylate, methyl acrylate, and fumaronitrile and describe some of their properties and their reactions with alcohol and with amines. Kropa and Nyquist[7] claim for the copolymer of methyl acrylate with propenyl isocyanate to impair special properties to textiles made of cotton, wool, and silk and also its use as binder for various fillers. Hart et al.[8] determined r_1 and r_2 for the copolymers of isopropenyl isocyanate with methyl acrylate and with styrene, and Fujisaki et al.[9] claim for its copolymer with acrylonitrile better dying properties in comparison to homopolyacrylonitrile. Butler and Monroe[10] prepared copolymers of both, β-allyloxyethyl isocyanate and of 9-decenyl isocyanate with methyl

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acrylate, styrene, and methyl methacrylate, and Graham[11] made graft copolymers from amine-terminated polystyrene with copolymers of β-isocyanatoethyl methacrylate. Vollmert[12] prepared impact-resistant polystyrene by joining a copolymer of styrene–isocyanatohexylacrylamide with a polyacrylate containing free carboxylic groups through the reaction of these carboxylic groups with the isocyanate groups of the styrene copolymer.

In the present paper, we wish to report the rather unique case of the dual synthesis of a copolymer which was obtained directly by radical-initiated copolymerization from two different starting monomer systems. Thus, only one type of copolymer, i.e., poly(styrene-co-styryl isocyanate), is obtained by copolymerization of styrene (S) either with cinnamoyl azide (CA) or with styryl isocyanate (SI):

CA   SI
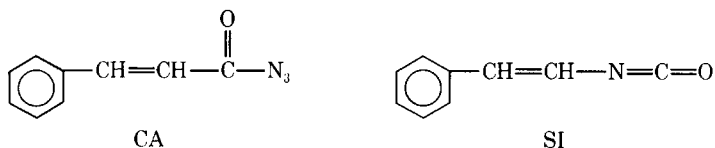
EXPERIMENTAL

Materials and Preparation of the Comonomers

Styrene was purified by washing with aqueous sodium hydroxide, drying, and subsequently distilling at reduced pressure. α,α'-Azodiisobutyronitrile (AIBN) was recrystallized from methanol.

Cinnamoyl Azide. The method of Naegli et al. for the preparation of acyl azides was used.[13] A solution of cinnamoyl chloride (30.0 g, 0.18 mole) in acetone (250 ml) was put in a three-necked flask fitted with stirrer and dropping funnel and placed in an ice bath. A solution of sodium azide (20.0 g, 0.31 mole) in distilled water (200 ml) was added through the dropping funnel to the stirred solution during 1 hr. Stirring was continued for 4 hr, and then the product was precipitated by the addition of cold distilled water (500 ml). The product, purified by recrystallization from ethanol (95%) and drying at 30°C at reduced pressure, melted under decomposition at 87°C. Lauder and Mason[14] report mp 86°C; yield, 70%.

Styryl Isocyanate.[14] A solution of cinnamoyl azide (20.0 g) in dry benzene (50 ml) was heated just below its boiling point for about 2 hr in a boiling flask fitted with a reflux condenser which was closed to the atmosphere by a calcium chloride tube. When the evolution of nitrogen had ceased, the benzene was distilled off and then the styryl isocyanate collected at 107°C/12 mm Hg (refractive index 1.592). Lauder and Mason[14] report bp 107°C/12 mm; yield, 70%.

Copolymerization. The copolymerizations of styrene with either cinnamoyl azide or with styryl isocyanate were carried out at 60°C as described before.[15] The total monomer feed in the reaction tubes was $M_1 + M_2 = 0.026$ mole, and the concentration of the initiator AIBN was 0.14 mole%. In the copolymerization of styrene with styryl isocyanate, weighing of the reactants and filling in the tubes was carried out in a dry-box. After the appropriate time of polymerization, the tubes were cooled down to −78°C and then opened and poured into ethanol (95%) for precipitation. The copolymers

TABLE I
Copolymerization of Styrene (M_1) with Cinnamoyl Azide (M_2)

Experiment no.	M_1, mole fraction of monomer 1	Time of polymerization, min	Conversion, %	Nitrogen content, %	m_1, mole fraction in copolymer	$[\eta]$, dl/g	T_g, °C	Melting range, °C
21/20	0.748	15	<0.5	1.97	0.844			
21/21	0.951	15	<0.5	0.64	0.951			
21/22	0.901	15	<0.5	1.12	0.914			
21/23	0.854	15	<0.5	1.50	0.883			
21/24	0.805	15	<0.5	1.70	0.867			
21/25	0.703	15	<0.5	2.38	0.809			
21/26	0.967	15	<0.5	0.56	0.957			
21/27	0.933	15	<0.5	0.83	0.937			
21/12	0.950	30	1.3	0.82	0.937	0.55		115–127
21/13	0.901	30	1.0	1.07	0.918	0.60		114–128
21/15	0.800	30	0.8	1.64	0.872	0.53		120–132
21/17	0.750	30	<0.5	2.18	0.827			
21/18	0.701	30	<0.5	2.43	0.805			
21/0	1.000	90	4.0	—	1.000	0.78	105	112–124
21/1	0.950	90	3.1	0.69	0.948	0.62		112–124
21/2	0.900	90	2.8	0.91	0.930	0.60		114–125
21/3	0.850	90	2.5	1.19	0.908	0.46		114–125
21/5	0.800	90	2.1	1.50	0.883	0.57		121–135
21/6	0.700	90	1.7	2.00	0.842			
22/0	1.000	450	16.5	—	1.000	0.7	105	
22/1	0.950	450	15.5	0.54	0.959	0.58	105	125–140
22/2	0.900	450	13.5	1.12	0.912	0.57	108	125–140
22/3	0.787	450	10.2	1.25	0.904	0.46	112	130–140
22/4	0.700	450	8.5	1.56	0.879	0.53	119	130–145
22/5	0.600	450	7.3	1.71	0.859	0.28	127	125–150

were purified by dissolving them in methyl ethyl ketone, followed by precipitation in ethanol (95%) and washing with petrol ether (40–60°C). They were dried at 60°C/0.1 mm Hg and obtained as colorless powder.

The composition of the copolymers was calculated from their nitrogen content.

The reaction conditions and results for the copolymerization of styrene with cinnamoyl azide are summarized in Table I and in Figures 1–3 and for the system styrene–styryl isocyanate in Table II and in Figures 4–6.

Physical Test Methods

Infrared Spectra. The infrared analyses were carried out on a Perkin-Elmer 237 grating infrared spectrometer with potassium bromide disks.
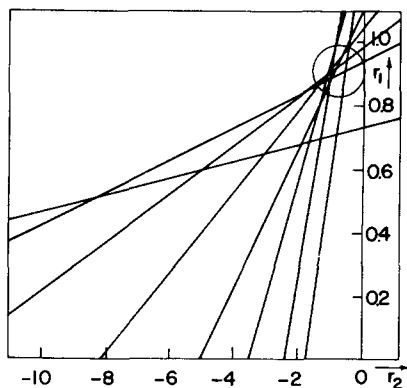

Fig. 1. Copolymerization of styrene (M_1) with cinnamoyl azide (M_2). Determination of r_1 and r_2.

Viscosity. The intrinsic viscosity of the copolymers was determined from viscosity measurements of their benzene solutions in an Ubbelohde viscometer at $25 \pm 0.05°C$ (Tables I and II).

Melting Range. The melting ranges were measured in capillaries with a temperature rise of about $4°C/min$.

Glass Transition Temperature. The glass transition temperature was determined by the method of Ellery[16] as described before,[17] using specimens which were moulded at room temperature at a pressure of 6000–8000 kg/cm^2.

Thermogravimetric Analysis. A modified helical-spring microbalance[18] was used for thermogravimetric analysis, working at a heating rate of $4°C/min$ in nitrogen atmosphere or in air.

Chemical Reactions of Poly(styrene-co-Styryl Isocyanate)

Reaction with an Alcohol (Ethanol). The copolymer (0.1 g) dissolved in dry benzene (10 ml) was refluxed with dry ethanol (2 ml) for 15 hr. The reaction product, precipitated by ethanol (95%), was filtered off, washed with petrol ether (bp 40–60°C), and dried at 80°C/0.1 mm Hg. Its infrared spectrum in KBr showed a new, strong absorption of the carbamate group at 1740 cm^{-1}, while the absorption of the isocyanate group at 2260 cm^{-1} became smaller (Fig. 7).
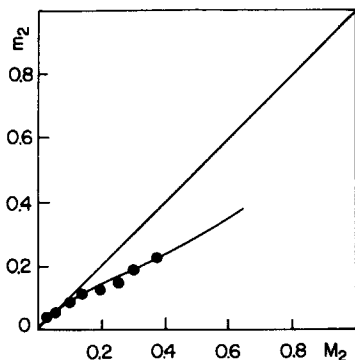

Fig. 2. Copolymerization of styrene (M_1) with cinnamoyl azide (M_2). Initial copolymer composition vs. composition of monomer feed.

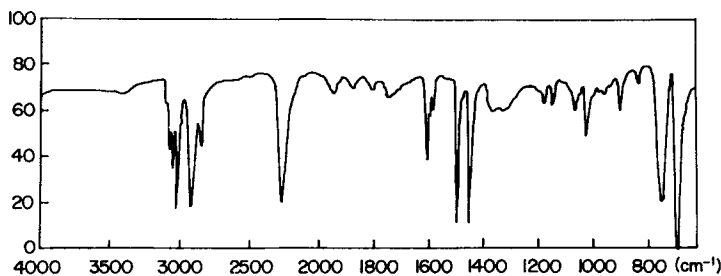Fig. 3. Infrared spectrum of poly(styrene-co-styryl isocyanate) obtained from copolymerization of styrene (M_1) with cinnamoyl azide (M_2).

TABLE II

Copolymerization of Styrene (M_1) with Styryl Isocyanate (M_2)

Experiment no.	M_1, mole fraction of monomer 1	Time of polymerization min	Conversion, %	Nitrogen content, %	m_1, mole fraction in copolymer	$[\eta]$, dl/g	T_g, °C	Melting range, °C
28/1	0.666	90	2.9	0.79	0.940			
28/2	0.754	90	1.1	0.575	0.958			
28/3	0.810	90	3.0	0.41	0.970	0.58	106	110–120
28/4	0.607	90	3.0	0.94	0.928			
28/5	0.653	90	2.2	0.72	0.945	0.56		105–117
28/6	0.692	90	2.8	0.62	0.953	0.57	105	110–120
28/7	0.532	90	2.1	1.10	0.915		103	105–117
28/10	0.345	90	2.0	1.98	0.844	0.54	120	130–140

Reaction with an Amine (*n*-Laurylamine). The copolymer (0.1 g) dissolved in dry benzene (10 ml) was refluxed with *n*-laurylamine (1.5 g) for 4 hr. After precipitation with petrol ether (40–60°C) and drying at 80°C/0.1 mm Hg, the reaction product showed a new, strong absorption of a substituted urea at 1660 cm^{-1} (in chloroform) (Fig. 8).

Reaction with a Diamine (1,5-Diaminopentane). The copolymer (0.1 g) dissolved in dry benzene (5 ml) was refluxed with 1,5-diaminopentane (10 mg). After 15 min, a white solid precipitated, which was washed with petrol ether (40–60°C) and dried at 80°C/0.1 mm. The infrared spectrum in KBr showed the typical absorption of a substituted urea at 1650–1700 cm^{-1}.

DISCUSSION

Both the radical-initiated bulk copolymerization of styrene (S) with cinnamoyl azide (CA) and of styrene (S) with styryl isocyanate (SI) yield the same copolymer type, i.e., poly(styrene-co-styryl isocyanate), having the isocyanate group attached to the alkylic polymer chain. Yet, as the reactivity parameters of the two systems obtained by the graphic method are quite different (system S–CA: $r_1 = 0.93 \pm 0.08$, $r_2 = -0.7 \pm 0.8$; system S–SI: $r_1 =$
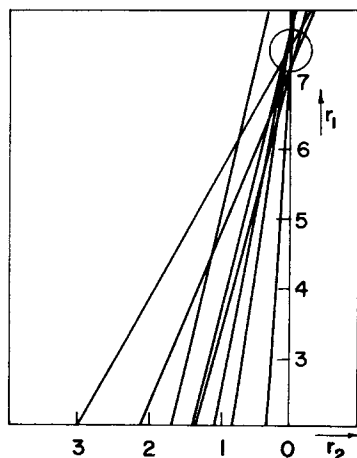

Fig. 4. Copolymerization of styrene (M_1) with styryl isocyanate (M_2). Determination of r_1 and r_2.

7.8 ± 0.6, r_2 = 0 ± 0.3) (Figs. 1 and 4), differently composed copolymers were obtained from monomer feeds with similar styrene content (Figs. 2 and 5).

Yet, in the determination of the copolymerization parameters for the pair styrene–cinnamoyl azide, the following two facts had to be taken into consideration:

1. At the temperature of polymerization, there occurs during the copolymerization concurrently a Curtius rearrangement of the cinnamoyl azide to styryl isocyanate. Thus, after 15 min at 60°C, ~8% of cinnamoyl azide is rearranged to styryl isocyanate, whereas after 30 min, ~17% of the acyl azide is rearranged. For this reason, copolymerization experiments for kinetic measurements were carried out as short as possible, explaining thus the rather low conversions of this series (Table I, experiments 21/20–21/27).

2. Both comonomers, the acyl azide and the isocyanate, react with styrene to give the same copolymer type, and no residual acyl azide groups were found in the copolymers obtained from the pair S–CA.

It was therefore necessary to understand the meaning of the r_1 and r_2 values of the systems S–CA.

The facts that the styryl radical reacts with cinnamoyl azide about ten times faster than with styryl isocyanate [eq. (1)],

$$\frac{r_1(\text{S-CA})}{r_1(\text{S-SI})} = \frac{k_{12}(\text{S-SI})}{k_{12}(\text{S-CA})} = \frac{0.93}{7.8} = 0.12 \tag{1}$$

and further, that only 8% of the acyl azide groups were converted to the isocyanate during the time of reaction (15 min) prove that it is the cinnamoyl
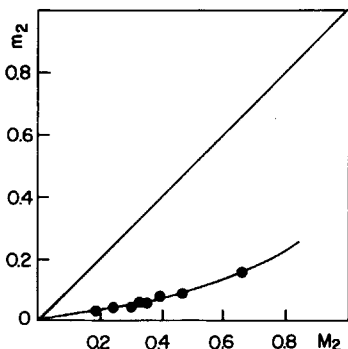

Fig. 5. Copolymerization of styrene (M_1) with styryl isocyanate (M_2). Initial copolymer composition vs. composition of monomer feed.
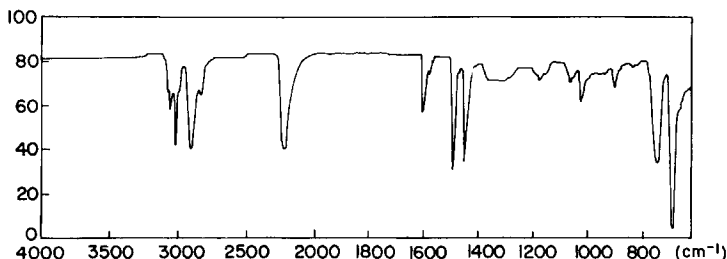

Fig. 6. Infrared spectrum of poly(styrene-co-styryl isocyanate) obtained from copolymerization of styrene (M_1) with styryl isocyanate (M_2).

azide which is involved in the propagation stage. Thus, the presence of iso-cyanate groups in the copolymers was actually only due to the rearrangement of the acyl azide groups after entering the polymer chain and only to a very small extent from the copolymerization of styrene with any styryl isocyanate formed during the time of reaction.

Regarding r_2(S–CA), the position is different, and the following possibilities are to be considered:

The expression $r_2 = (k_{22}/k_{21})$ (S–CA) is only correct if the rate of the rearrangement k_R of the acyl azide radical to the isocyanate radical is much smaller than the rate of propagation, $k_R \ll k_{21}$. If, however, $k_R \simeq k_{21}$, three types of chain radicals will take part in the propagation, i.e., the styryl, the acyl azide, and the newly formed isocyanate radical. The third possibility, which as shown further on seems to be the correct one, can be explained in two ways:

1. The rearrangement of the acyl azide to the isocyanate is much faster than the propagation step, i.e., $k_R \gg k_{21}$. For this case, the overall propagation can be expressed by the following five equations, (2), where $\sim M_3\cdot$ means the styryl isocyanate radical in the growing chain:

$$\sim M_1\cdot\ +\ M_1\ \xrightarrow{k_{11}}\ \sim M_1 M_1\cdot$$

$$\sim M_1\cdot\ +\ M_2\ \xrightarrow{k_{12}}\ \sim M_1 M_2\cdot$$

$$\sim M_2\cdot\ \xrightarrow{k_R}\ \sim M_3\cdot \qquad\qquad (2)$$

$$\sim M_3\cdot\ +\ M_1\ \xrightarrow{k_{31}}\ \sim M_3 M_1\cdot$$

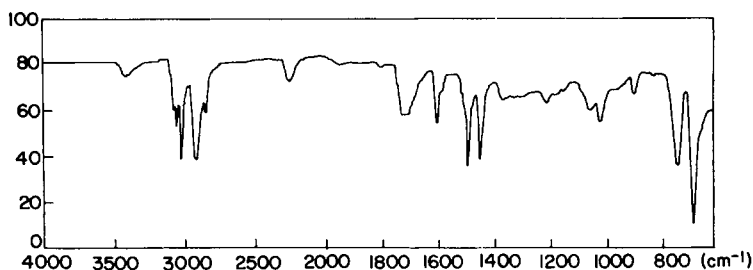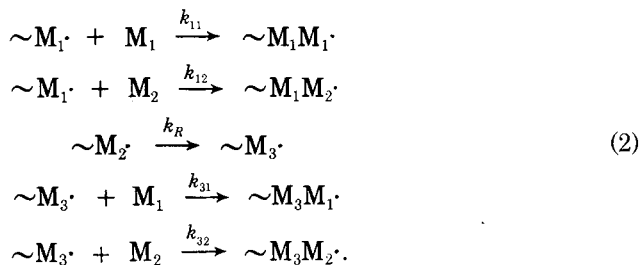$$\sim M_3\cdot\ +\ M_2\ \xrightarrow{k_{32}}\ \sim M_3 M_2\cdot.$$

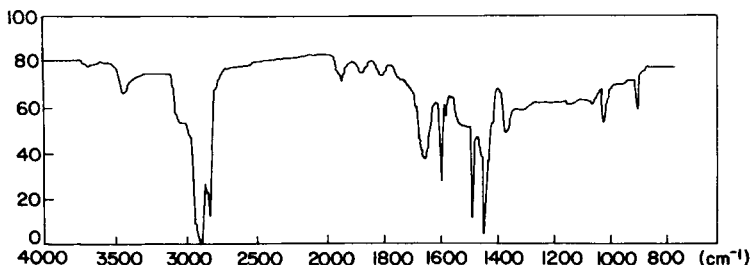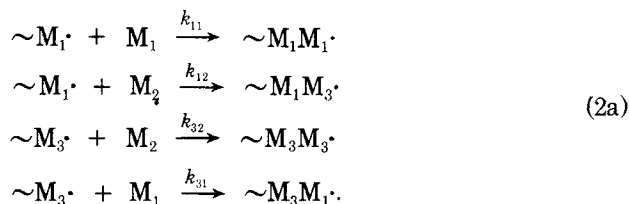Fig. 7. Infrared spectrum of poly(styrene-co-styryl isocyanate) after reaction with ethanol.

Fig. 8. Infrared spectrum of poly(styrene-co-styryl isocyanate) after reaction with n-laurylamine.

2. There is no formation of the radical $M_2 \cdot$ at all, and cinnamoyl azide (M_2) is rearranged to the styryl isocyanate radical ($M_3 \cdot$) simultaneously during the attachment of the growing chain. In this case, the overall propagation is given by the following four equations, (2a):

$$
\begin{aligned}
\sim M_1 \cdot \; + \; M_1 \; &\xrightarrow{k_{11}} \; \sim M_1 M_1 \cdot \\
\sim M_1 \cdot \; + \; M_2 \; &\xrightarrow{k_{12}} \; \sim M_1 M_3 \cdot \\
\sim M_3 \cdot \; + \; M_2 \; &\xrightarrow{k_{32}} \; \sim M_3 M_3 \cdot \\
\sim M_3 \cdot \; + \; M_1 \; &\xrightarrow{k_{31}} \; \sim M_3 M_1 \cdot .
\end{aligned}
\tag{2a}
$$

For both mechanisms, the rates of consumption of the monomers are

$$
\frac{-d[M_1]}{dt} = k_{11}[M_1 \cdot][M_1] + k_{31}[M_3 \cdot][M_1]
\tag{3}
$$

$$
\frac{-d[M_2]}{dt} = k_{12}[M_1 \cdot][M_2] + k_{32}[M_3 \cdot][M_2]
\tag{4}
$$

and, at steady state, it can be assumed that

$$
k_{12}[M_1 \cdot][M_2] = k_{31}[M_3 \cdot][M_1] .
\tag{5}
$$

Dividing eq. (3) by eq. (4) and eliminating the concentration of the radicals by the use of eq. (5), eq. (6) is obtained:

$$
\frac{d[M_1]}{d[M_2]} = \frac{\dfrac{k_{11}[M_1]}{k_{12}[M_2]} + 1}{\dfrac{[M_1]}{[M_2]} + \dfrac{k_{32}}{k_{31}}} \frac{[M_1]}{[M_2]}.
\tag{6}
$$

Using the linear form of eq. (6), the copolymerization parameters r_1 and r_2 were determined by the graphic method.[19] Thus, for the pair styrene–cinnamoyl azide, r_1 and r_2 are defined as follows:

$$
r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{32}}{k_{31}} .
\tag{7}
$$

The reasons for our considering the third possibility as the right one are the following: First, no traces of the acyl azide were found in the copolymer. If the copolymerization proceeds by mechanism (2), in comparison with the conjugated monomer, rearrangement could be accelerated owing to the loss of conjugation of the acyl azide with the aromatic ring after entering the polymer chain and also owing to the strong inductive effect of the polymer chain.

Considering mechanism (2a), the bond between the $=CH-$ and the $-\overset{\overset{\textstyle O}{\|}}{C}-N_3$ group of the comonomer CA will be weakened by the attack of the chain radical, resulting in rearrangement and propagation simultaneously. At this stage, it is not possible to decide which mechanism is the correct one.

Comparing the comonomer content in the copolymer obtained from the various starting mixtures of the pair styrene–cinnamoyl azide, one can ob-

serve a decrease at reaction times of 90 and 450 min (Table I). This can be explained by the fact that, in these cases, a considerable part of the cinnamoyl azide has already rearranged to styryl isocyanate, which enters into the copolymer to a much lesser extent. Thus, after prolonged reaction times, three monomers, styrene, cinnamoyl azide, and styryl isocyanate, terpolymerize to the copolymer poly(styrene-co-styryl isocyanate). One can say that the resulting copolymer is composed of blocks, richer or poorer in their isocyanate content depending on whether they were formed from the pair S–CA or from the pair S–SI.

For the system S–CA, there exists a more or less azeotropic range up to a content of about 10 mole-% cinnamoyl azide in the monomer feed, i.e., up to about 10 mole-% of styryl isocyanate in the copolymer (Fig. 2), whereas for the system S–SI, the isocyanate content of the copolymer is always lower than in the monomer feed (Fig. 5).

Characterization of the Copolymers

The infrared spectra of copolymers obtained from styrene with cinnamoyl azide (Fig. 3) are identical to that of the copolymer made from the system styrene–styryl isocyanate (Fig. 6).

All the copolymers, like homopolystyrene, are soluble in toluene, MEK, etc.

Also, the thermal stability of the copolymers is similar to that of polystyrene, and they start to decompose at ~325°C in nitrogen and at ~300°C in air.

Chemical Reactions of the Copolymer

The obtained copolymers, although containing the rather reactive isocyanate group, are quite stable at normal conditions, and no changes were observed after storage for several months, as indicated by unchanged infrared spectra. This high stability of the isocyanate groups against moisture and against cold ethanol, which was used for precipitation of the copolymer from its solution in MEK, can be explained by steric hindrance of the secondary isocyanate and further by the inductive effect of the main chain.

By heating the copolymer with alcohol or with an amine, the corresponding reaction products were obtained. Thus, with ethanol, most of the isocyanate groups were transformed to ethyl carbamate groups, $\sim NH\text{-}\overset{\text{O}}{\underset{\|}{C}}\text{-O-}CH_2CH_3$, as verified by the typical infrared absorption of the carbonyl group of a carbamate at 1740 cm^{-1} (Fig. 7).[20] Yet, after refluxing with ethanol even for 15 hr, there remain still some free isocyanate groups, and consequently the corresponding infrared absorption at 2260 cm^{-1}, although much weaker than in the original copolymer, is still visible. The reaction with amines is much faster than with alcohol, and after reacting with n-laurylamine, the copolymer showed the typical absorption band of the carbonyl group of a substituted urea at 1660 cm^{-1} (Fig. 8),[20] while the bands of the isocyanate group had disappeared. Reacting with a diamine, 1,5-diaminopentane, crosslinking occurs, and the obtained product is insoluble in toluene, MEK, DMF, etc. As

with the monoamine, a new, wide band of a substituted urea at 1650–1700 cm^{-1} appeared[20] with the simultaneous disappearance of the band of the isocyanate group at 2260 cm^{-1}.

Summarizing, the new poly(styrene-co-styryl isocyanate) can be grafted or crosslinked through the lateral isocyanate groups, and colored copolymers can be obtained by internal dying. Further, the copolymers could be used as matrix to attach enzymes and as carriers for slow release pharmaceuticals, insecticides, etc.

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