

Terpolymerization Studies. I. Terpolymerization of Acrylonitrile, Styrene, and Esters of α -Cyanocinnamic Acid

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Synopsis

The terpolymerizations of acrylonitrile, styrene, and seven esters of α -cyanocinnamic acid were investigated up to low conversions. Polymerizations, carried out in bulk at 70°C, were initiated by free radicals. The relationships between monomer feed and terpolymer composition were determined on a triangular coordinate graph as proposed by Slocombe. In all cases, there exists an azeotropic line, connecting the binary azeotrope of the pair acrylonitrile-styrene and that of the various pairs of styrene with the esters of α -cyanocinnamic acid, yet no real ternary azeotrope was found.

INTRODUCTION

The growth in the production of plastic materials during the past few years has been accompanied by an increased demand for materials with improved physical and mechanical properties, greater heat and radiation stability, etc. Only a few known homopolymers answer such demands. As a result, there have been rapid developments in the fields of polymer blends, graft polymers, and copolymerizations of two or more monomers.

In the present paper, the terpolymerizations of acrylonitrile ($A = M_1$), styrene ($S = M_2$), and a number of esters of α -cyanocinnamic acid (CC) (M_3) are reported. The esters used are methyl (MeCC), ethyl (EtCC), *n*-butyl (BuCC), *n*-hexyl (*n*-HeCC), cyclohexyl (*c*-HeCC), benzyl (BeCC), and 2-ethylhexyl (EtHeCC) esters. The binary copolymerizations of these esters with styrene^{1,2} and of the methyl (MeCC) and ethyl (EtCC) ester with acrylonitrile^{2,3} and some of the physical and mechanical properties of these copolymers have been studied previously.^{4,5,6}

EXPERIMENTAL

Materials and Preparation of Monomers

Acrylonitrile. Commercial Eastman product was dried over calcium chloride and distilled before use under nitrogen at 77°C. The distillate was kept at Dry-Ice temperature until used.

Styrene. Practical Eastman product was purified by washing with aque-

ous sodium hydroxide, drying, and distilling at reduced pressure. The distillate was kept at Dry-Ice temperature until used.

Benzoyl Peroxide. Eastman pure grade was used after recrystallization from methanol.

Comonomers. Details of the syntheses of the methyl, ethyl, *n*-butyl, *n*-hexyl, cyclohexyl, 2-ethylhexyl, and benzyl esters of α -cyanocinnamic acid were reported previously.^{1,2}

Terpolymerization.

In order to determine the molar composition of the obtained terpolymers in relation to the corresponding compositions of monomer feed, polymerization experiments were carried out in bulk in the manner described before,¹ using benzoyl peroxide (0.1% of monomer mixture) as initiator.

The terpolymerizations were carried out in a temperature-controlled bath, fitted with shaking device in order to keep the reaction mixtures well mixed. At the fixed polymerization temperature ($70^\circ \pm 0.5^\circ\text{C}$), the starting reaction mixtures were homogeneous solutions. The proper time of polymerization, i.e., the time necessary to polymerize not more than 10% of the mixture, was found by trial and error. After the polymerization, the reaction tubes were cooled to room temperature, opened, and the reaction mixtures were poured into methanol. The filtered products were washed with methanol and repeatedly precipitated in a Waring Blendor by methanol from a solution in methyl ethyl ketone. The purified terpolymers were dried at 80°C under reduced pressure during 24 hr. All the terpolymers were obtained as white powders.

Analyses of Products

The composition of the terpolymers was determined by elemental analysis of their nitrogen and oxygen contents.

Details on the conditions of the terpolymerization experiments and the results are summarized in Tables I to VII.

The relationship between the composition of the terpolymers and the monomer feed is depicted by Slocombe's triangle method,⁷ plotting monomer feed and polymer composition on a triangular coordinate graph. Connecting the corresponding points, the arrowhead indicates the initial terpolymer composition obtained from a monomer feed as indicated by the tail of the arrow (Figs 1-7).

Melting Range

The melting range of the obtained terpolymers, defined as the range of temperature when the first changes in the shape of the white polymer particles occur and the temperature when the polymer particles coalesce into a continuous phase, was determined in capillaries or on a hot stage microscope.

Glass Transition Temperature

The glass transition temperature was determined according to the method of Ellery,⁸ by recording the penetration curve of a needle into the polymer specimen at raising temperature.

TABLE I
 Terpolymerization of Acrylonitrile (M_1), Styrene (M_2), and Methyl α -Cyanocinnamate (M_3)

Experiment no.	Monomer feed mole fraction			Time, min	Conversion, %	N, %	O, %	Mole fraction			Melting range, °C	T_g , °C
	M_1	M_2	M_3					m_1	m_2	m_3		
14/1	0.80	0.10	0.10	125	3.9	11.78	1.18	0.606	0.366	0.028	170-218	116
14/2	0.60	0.30	0.10	110	4.2	8.11	1.81	0.446	0.506	0.047	180-210	118.5
14/3	0.25	0.65	0.10	60	3.8	5.63	2.29	0.310	0.623	0.066	180-209	134
14/4	0.10	0.80	0.10	80	2.8	3.56	2.59	0.176	0.741	0.083		132
14/5	0.70	0.10	0.20	70	5.9	10.50	1.22	0.556	0.414	0.029	175-221	117
14/6	0.50	0.30	0.20	70	4.4	6.82	1.98	0.346	0.603	0.050	165-218	131.5
14/7	0.30	0.50	0.20	70	5.7	5.52	2.80	0.294	0.622	0.083		135
14/8	0.10	0.70	0.20	110	1.9	4.63	4.81	0.193	0.645	0.161		
14/9	0.60	0.10	0.30	110	2.8	9.40	2.98	0.494	0.426	0.079	175-213	
14/10	0.40	0.30	0.30	70	5.5	6.38	3.98	0.346	0.533	0.120	195-234	
14/11	0.10	0.60	0.30	75	4.5	3.92	5.87	0.112	0.673	0.212	205-240	166.5
14/12	0.40	0.20	0.40	75	4.1	6.60	4.62	0.322	0.535	0.142		
14/13	0.10	0.50	0.40	70	5.9	4.19	6.73	0.106	0.643	0.251	195-258	
51/1	0.05	0.90	0.05	95	2.3	2.86	2.51	0.131	0.787	0.081	199-203	126.5
51/2	0.05	0.80	0.15	80	3.2	3.45	4.82	0.108	0.723	0.169	175-226	153
51/3	0.20	0.75	0.05	80	3.5	4.68	1.59	0.268	0.685	0.046	160-202	112.5
51/4	0.30	0.65	0.05	80	5.5	5.66	1.26	0.329	0.635	0.035	160-203	116
51/5	0.20	0.70	0.10	80	4.6	4.88	2.54	0.261	0.662	0.076		127
51/6	0.10	0.75	0.15	75	5.0	3.81	4.80	0.149	0.705	0.145	170-225	146
51/7	0.05	0.75	0.20	65	3.9	3.43	5.58	0.083	0.714	0.203		163

TABLE II
 Terpolymerization of Acrylonitrile (M_1), Styrene (M_2), and Ethyl α -Cyanocinnamate (M_3)

Experiment no.	Monomer feed mole fraction			Time, min	Conversion, %	N, %	O, %	Mole fraction			Melting range, °C	T_g , °C
	M_1	M_2	M_3					m_1	m_2	m_3		
	Terpolymer											
13/1	0.80	0.10	0.10	80	7.5	10.67	1.04	0.567	0.409	0.025	180-213	
13/2	0.60	0.30	0.10	80	7.0	7.51	2.03	0.499	0.434	0.066	180-210	
13/3	0.40	0.50	0.10	80	5.5	6.25	1.42	0.359	0.601	0.039	185-212	120.5
13/4	0.20	0.71	0.09	120	3.5	4.69	2.28	0.252	0.680	0.068	185-215	
13/5	0.60	0.20	0.20	80	8.1	8.61	1.95	0.471	0.477	0.052		125.5
13/6	0.40	0.40	0.20	80	7.7	6.82	3.54	0.360	0.533	0.106		128.5
13/7	0.20	0.60	0.20	80	4.4	5.30	4.86	0.243	0.593	0.163	195-221	154
13/8	0.10	0.60	0.30	120	4.5	4.10	3.83	0.182	0.693	0.125		130
13/9	0.60	0.10	0.30	80	6.2	9.49	2.24	0.509	0.432	0.059		131.5
13/10	0.46	0.23	0.31	80	7.6	7.06	3.53	0.374	0.521	0.104		
13/11	0.10	0.40	0.50	80	4.0	4.56	7.29	0.123	0.592	0.285	190-259	174

TABLE III
 Terpolymerization of Acrylonitrile (M_1), Styrene (M_2), and *n*-Butyl α -Cyanocinnamate (M_3)

Experiment no.	Monomer feed mole fraction			Time, min	Conversion, %	N, %	O, %	Terpolymer			Melting range, °C	T_g , °C
	M_1	M_2	M_3					Mole fraction				
								m_1	m_2	m_3		
52/1	0.05	0.90	0.05	108	4.8	2.56	2.22	0.121	0.805	0.074		
52/2	0.05	0.80	0.15	104	5.5	3.08	4.47	0.097	0.736	0.166		
52/3	0.20	0.75	0.05	64	3.7	4.60	1.44	0.270	0.686	0.043		111.5
52/4	0.30	0.65	0.05	80	4.8	5.54	1.21	0.327	0.638	0.034		
52/5	0.20	0.70	0.10	76	4.0	4.58	2.47	0.251	0.671	0.077		119
52/7	0.05	0.75	0.20	98	1.7	3.20	5.00	0.088	0.719	0.192	175-240	129.5
52/8	0.25	0.65	0.10	93	6.0	5.06	2.16	0.297	0.638	0.067	165-208	119.5
52/10	0.50	0.30	0.20	69	4.4	6.00	3.09	0.328	0.576	0.095	170-222	
52/13	0.50	0.45	0.05	53	1.3	7.47	0.89	0.429	0.546	0.024		
52/14	0.43	0.51	0.06	45	3.3	6.70	1.14	0.389	0.579	0.031	175-207	

TABLE IV
 Terpolymerization of Acrylonitrile (M_1), Styrene (M_2), and *n*-Hexyl α -Cyanocinnamate (M_3)

Experiment no.	Monomer feed mole fraction			Time, min	Conversion, %	N, %	O, %	Terpolymer			Melting range, °C	T_g , °C
	M_1	M_2	M_3					Mole fraction				
								m_1	m_2	m_3		
17/1	0.80	0.10	0.10	50	3.7	11.05	0.97	0.579	0.398	0.023	150-218	
17/2	0.58	0.32	0.10	50	5.1	7.83	1.10	0.449	0.521	0.029	145-207	
17/3	0.40	0.50	0.10	67	5.0	6.26	2.39	0.353	0.572	0.071	150-207	
17/4	0.10	0.80	0.10	90	4.4	3.40	2.76	0.180	0.737	0.093	145-195	
17/5	0.78	0.11	0.11	50	5.1	10.42	0.73	0.559	0.422	0.018		110.5
17/6	0.56	0.33	0.11	50	4.5	7.57	1.27	0.436	0.530	0.034		112.5
17/7	0.33	0.56	0.11	90	4.9	5.72	1.89	0.326	0.618	0.055	147-206	
17/8	0.11	0.78	0.11	70	3.4	3.59	3.05	0.164	0.721	0.103		113.5
17/9	0.60	0.10	0.30	50	4.4	8.85	2.58	0.495	0.421	0.070		
17/10	0.40	0.30	0.30	35	4.5	6.04	3.01	0.332	0.550	0.118		
17/11	0.10	0.60	0.30	110	3.9	3.66	5.11	0.131	0.664	0.204	155-215	118.5
17/12	0.40	0.20	0.40	35	4.0	6.57	3.80	0.358	0.521	0.120		
17/13	0.10	0.50	0.40	60	5.0	3.62	5.38	0.118	0.659	0.221		

TABLE V
 Terpolymerization of Acrylonitrile (M_1), Styrene (M_2), and Cyclohexyl α -Cyanocinnamate (M_3)

Experiment no.	Monomer feed mole fraction			Time, min	Conversion, %	N, %	O, %	Terpolymer			Melting range, °C	T_g , °C
	Mole fraction							Mole fraction				
	M_1	M_2	M_3					m_1	m_2	m_3		
16/1	0.80	0.10	0.10	55	2.8	11.10	1.23	0.591	0.378	0.030	150-218	
16/2	0.60	0.30	0.10	35	3.7	7.91	1.18	0.453	0.516	0.031	155-218	115.5
16/3	0.40	0.50	0.10	40	4.4	6.23	2.87	0.354	0.560	0.085	155-215	
16/4	0.10	0.80	0.10	65	5.1	3.36	3.59	0.148	0.721	0.130	175-218	130
16/5	0.70	0.10	0.20	35	3.6	9.92	1.07	0.542	0.431	0.026		
16/7	0.39	0.435	0.175	40	2.9	5.92	3.17	0.332	0.566	0.101	160-218	121
16/8	0.10	0.70	0.20	55	4.4	3.45	4.72	0.124	0.691	0.184		
16/9	0.60	0.10	0.30	65	4.5	8.88	5.60	0.492	0.319	0.187	160-221	
16/10	0.40	0.30	0.30	35	3.4	6.05	3.40	0.332	0.560	0.108		
16/11	0.10	0.60	0.30	40	2.6	3.53	5.00	0.122	0.667	0.199	180-242	
16/12	0.40	0.20	0.40	65	5.3	3.36	4.29	0.129	0.706	0.164		142.5
16/13	0.10	0.50	0.40	35	2.3	3.66	5.56	0.115	0.656	0.227	185-243	

TABLE VI
 Terpolymerization of Acrylonitrile (M_1), Styrene (M_2), and Benzyl α -Cyanocinnamate (M_3)

Experiment no.	Monomer feed mole fraction			Time, min	Conversion, %	N, %	O, %	Terpolymer			Melting range, °C	T_g , °C
	M_1	M_2	M_3					m_1	m_2	m_3		
15/1	0.80	0.10	0.10	65	4.8	10.16	1.26	0.554	0.414	0.031	160-205	116
15/2	0.60	0.30	0.10	50	4.8	7.84	1.29	0.449	0.515	0.034	155-203	
15/3	0.40	0.50	0.10	65	6.1	6.21	1.52	0.365	0.591	0.043	180-205	
15/4	0.10	0.80	0.10	65	6.2	3.34	2.81	0.165	0.739	0.096	162-209	124
15/5	0.70	0.10	0.20	35	3.9	9.53	1.50	0.527	0.433	0.039		
15/6	0.50	0.30	0.20	35	4.6	6.55	2.00	0.380	0.571	0.048		
15/7	0.30	0.50	0.20	50	2.3	5.40	3.61	0.300	0.578	0.122		124
15/8	0.10	0.70	0.20	50	4.0	3.52	4.96	0.122	0.679	0.198		
15/9	0.60	0.10	0.30	65	3.5	8.17	3.47	0.449	0.449	0.102	155-222	
15/10	0.40	0.30	0.30	65	3.2	5.98	3.70	0.331	0.546	0.122	180-218	148
15/11	0.10	0.60	0.30	50	4.9	3.56	5.51	0.111	0.656	0.233		
15/12	0.40	0.20	0.40	50	5.9	6.16	4.71	0.325	0.510	0.164	175-234	

TABLE VII
 Terpolymerization of Acrylonitrile (M_1), Styrene (M_2), and 2-Ethylhexyl α -Cyanocinnamate (M_3)

Experiment no.	Monomer feed mole fraction			Time, min	Conversion, %	N, %	O, %	Terpolymer			Melting range, °C	T_g , °C
	M_1	M_2	M_3					Mole fraction				
								m_1	m_2	m_3		
53/1	0.05	0.90	0.05	105	4.8	2.56	2.06	0.129	0.799	0.070	135-191	
53/2	0.05	0.80	0.15	88	5.0	2.90	4.68	0.088	0.714	0.197		
53/3	0.20	0.75	0.05	85	6.5	4.81	1.34	0.291	0.668	0.040	150-203	
53/4	0.30	0.65	0.05	55	3.7	5.76	1.02	0.347	0.623	0.029	135-205	
53/5	0.20	0.70	0.10	85	3.8	4.80	2.22	0.280	0.649	0.070		
53/6	0.10	0.75	0.15	83	5.4	3.61	3.70	0.171	0.690	0.138		109
53/7	0.05	0.75	0.20	105	5.4	3.13	4.82	0.105	0.674	0.219	175-208	113
53/8	0.25	0.65	0.10	60	2.8	5.25	1.97	0.311	0.628	0.060	165-202	
53/9	0.50	0.30	0.20	28	1.9	7.07	2.35	0.413	0.516	0.069		
53/10	0.10	0.50	0.40	45	2.5	3.66	5.69	0.061	0.676	0.263		
53/11	0.20	0.60	0.20	100	6.3	4.34	3.49	0.231	0.643	0.125	180-202	
53/12	0.30	0.50	0.20	80	5.4	5.36	2.89	0.308	0.596	0.095		110
53/14	0.70	0.25	0.05	50	4.7	8.91	0.79	0.502	0.478	0.019	170-206	113

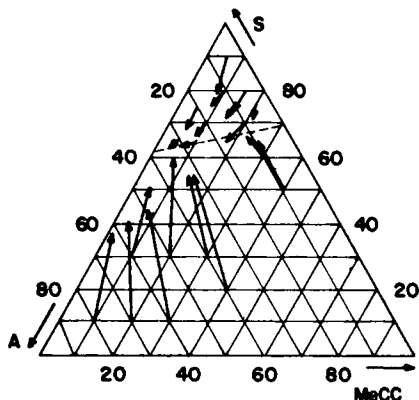


Fig. 1. Monomer-terpolymer triangular composition plots for the system acrylonitrile-styrene-methyl α -cyanocinnamate.

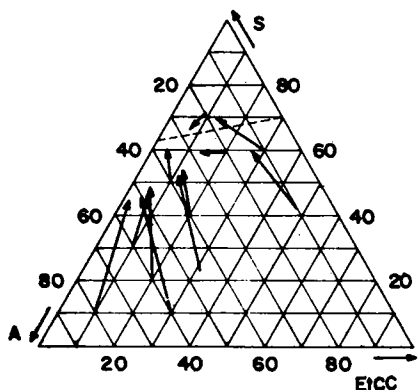


Fig. 2. Monomer-terpolymer triangular composition plots for the system acrylonitrile-styrene-ethyl α -cyanocinnamate.

The needle had a circular cross section of 1 mm^2 and carried a weight of 2 kg. The temperature of the silicon oil bath was raised uniformly at a rate of 2°C per minute. The curve of depth of penetration against the temperature was obtained directly on a recording instrument.

The terpolymer specimens, which had diameters of about 5 mm and heights of 2–3 mm, were either molded under pressure at the appropriate temperature or cut from cast resin.

Viscosity

Intrinsic viscosities of the terpolymers were determined from measurements in methyl ethyl ketone in a Ubbelohde viscometer at $30^\circ \pm 0.1^\circ\text{C}$. The values obtained are in the range of $[\eta] \approx 0.8\text{--}1.5 \text{ dl/g}$, indicating the high molecular weight of the terpolymers.

IR Spectra

Infrared analyses were carried out on a Perkin-Elmer 237 grating infrared spectrophotometer, using the terpolymers either in powder form in ad-

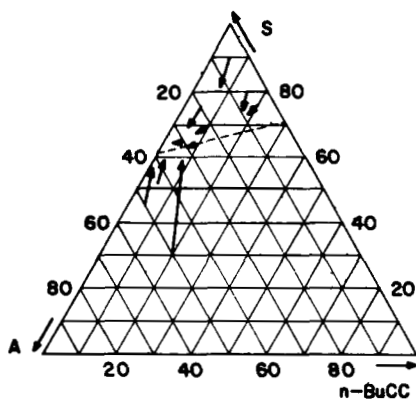


Fig. 3. Monomer-terpolymer triangular composition plots for the system acrylonitrile-styrene-*n*-butyl α -cyanocinnamate.

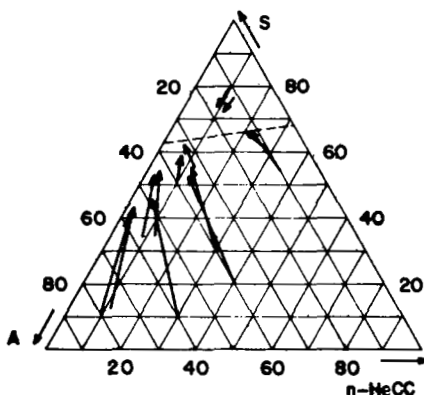


Fig. 4. Monomer-terpolymer triangular composition plots for the system acrylonitrile-styrene-*n*-hexyl α -cyanocinnamate.

mixture with KBr or as films, which were obtained by solvent evaporation from dilute solutions. A typical example for one of the terpolymers (A—S—EtCC) is given in Figure 8.

Thermogravimetric Analysis

Thermogravimetric analyses were carried out on a semiautomatic helical spring microbalance⁹ by heating the polymer samples at a predetermined rate up to about 450°C in nitrogen.

All the terpolymers, obtained in bulk to low conversion, were soluble in ketones, aromatics, and in chlorinated solvents.

RESULTS AND DISCUSSION

Terpolymerization

The relationship between the molar composition of the various terpolymers—determined by elemental analysis—and the corresponding composition of monomer feed is represented in the form of triangular plots (Figs 1–7).

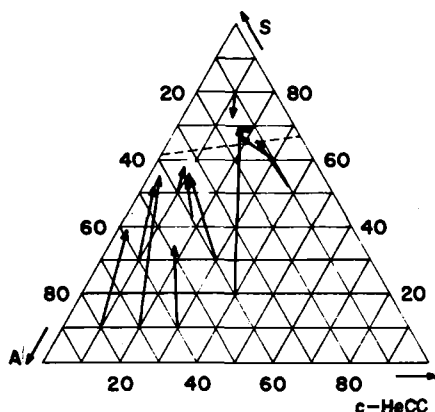


Fig. 5. Monomer-terpolymer triangular composition plots for the system acrylonitrile-styrene-cyclohexyl α -cyanocinnamate.

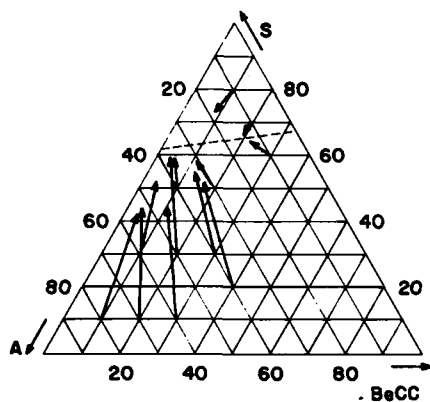


Fig. 6. Monomer-terpolymer triangular composition plots for the system acrylonitrile-styrene-benzyl α -cyanocinnamate.

As all experiments were carried out at the same conditions, the influence of the various ester types at equal molar composition can be studied. One can observe in all cases that the arrows point toward a quite well-defined line, which corresponds to the connecting line between the binary azeotropic compositions of the pairs acrylonitrile-styrene and styrene- α -cyanocinnamate, designated by Slocombe⁷ as the azeotropic line, and that the arrows are inclined more in the direction of the azeotropic composition of the pair acrylonitrile-styrene ($m_1/m_2 = 38.5/61.5$).¹⁰ Further, the arrows get shorter when located near the azeotropic line, indicating that the composition of the terpolymers are quite similar to that of the monomer feed.

This azeotropic line of Slocombe, whose importance will be shown also later on, has some significance in respect to styrene. One can observe in all diagrams that in the region between the azeotropic line and the apex of styrene, the concentration of styrene in the terpolymers is lower than in the starting monomer mixtures, whereas for all other starting compositions there is an increase of the styrene content in the terpolymers. Further, the molar proportion of each monomer in the terpolymer does not vary randomly, but depends on the starting composition.

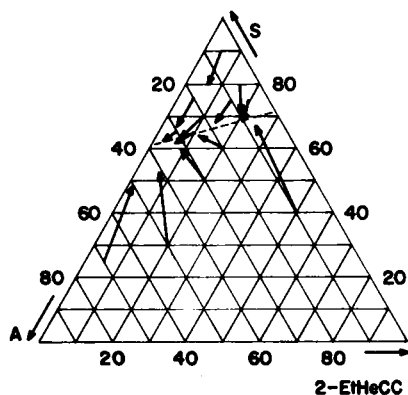


Fig. 7. Monomer-terpolymer triangular composition plots for the system acrylonitrile-styrene-2-ethylhexyl α -cyanocinnamate.

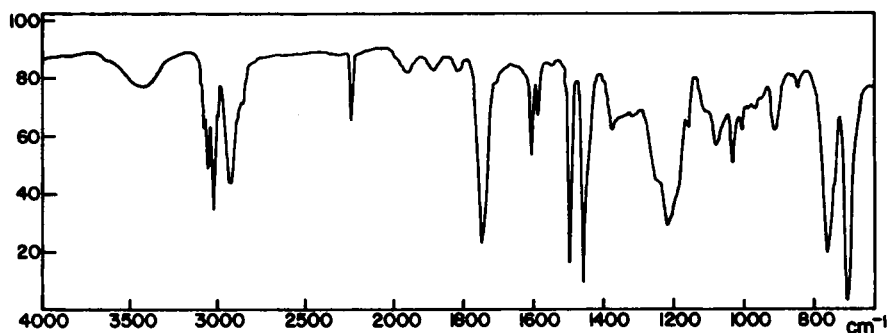


Fig. 8. Infrared spectrum of terpolymer acrylonitrile-styrene-ethyl α -cyanocinnamate.

All the polymerization experiments were carried out up to low conversions only, and consequently one can assume that there occurred no significant change in the composition of the monomer mixtures, thus permitting the use of the terpolymer equations of Alfrey and Goldfinger.¹¹

Generally, in the radical terpolymerization of the monomers M_1 , M_2 , and M_3 , there exist three types of active growing chain ends, $-m_1'$, $-m_2'$, and $-m_3'$, and each of these ends can react with any one of the three monomers present. Consequently, chain growth occurs according to nine propagation reactions from which the basic equations of terpolymer composition were derived. But as the ester comonomers of the present investigation do not homopolymerize ($k_{33} = 0$), i.e., $r_{31} = r_{32} = 0$, the corresponding modified eqs. (1), relating the composition of the terpolymer to the monomer mixture, are to be applied, where $R = k_{31}/k_{32}$ is unknown¹²:

$$d[M_1]:d[M_2]:d[M_3] = m_1:m_2:m_3 =$$

$$[M_1] \left\{ R \frac{[M_1]}{r_{21}} + \frac{[M_2]}{r_{21}} + R \frac{[M_3]}{r_{23}} \right\} \left\{ [M_1] + \frac{[M_2]}{r_{12}} + \frac{[M_3]}{r_{13}} \right\}$$

$$:[M_2] \left\{ R \frac{[M_1]}{r_{12}} + \frac{[M_2]}{r_{12}} + \frac{[M_3]}{r_{13}} \right\} \left\{ \frac{[M_1]}{r_{21}} + [M_2] + \frac{[M_3]}{r_{23}} \right\} \quad (1)$$

$$:[M_3] \left\{ \frac{[M_1]}{r_{13}r_{21}} + \frac{[M_2]}{r_{12}r_{23}} + \frac{[M_3]}{r_{13}r_{23}} \right\} \{ R[M_1] + [M_2] \}.$$

TABLE VIII
Copolymerization Parameters and e and Q Values for Esters
of α -Cyanocinnamic Acid (M_3) with Styrene (M_2)

Ester group in M_3	r_{23}	e_3	Q_3	Reference
Methyl-	0.45	2.49	0.14	2
Ethyl-	0.51	2.44	0.14	1,3
<i>n</i> -Butyl-	0.53	2.42	0.14	2
<i>n</i> -Hexyl-	0.42	2.58	0.16	2
Cyclohexyl-	0.44	2.56	0.15	2
2-Ethylhexyl-	0.59	2.36	0.13	2
Benzyl	0.43	2.57	0.15	2

TABLE IX
Calculated Mean Value of R

Terpolymer	R	Number of experiments for calculations of R
A-S-MeCC	0.40	22
A-S-EtCC	0.43	5
A-S-BuCC	0.33	13
A-S- <i>n</i> -HeCC	0.47	12
A-S- <i>c</i> -HeCC	0.44	6
A-S-BeCC	0.31	7
A-S-EtHeCC	0.34	7

The values of r_{12} , r_{21} , r_{13} , and r_{23} are known from binary copolymerizations. Thus for the pair acrylonitrile-styrene, the values $r_{12} = 0.04 \pm 0.04$ and $r_{21} = 0.41 \pm 0.08$ were chosen.¹⁰ The monomer reactivity ratios r_{23} of styrene with the different ester comonomers were reported before² and are given in Table VIII, whereas only one value, $r_{13} = 18$, was applied for all pairs of acrylonitrile with the various esters.²

The mean values of R , taking into account only positive R values, were calculated from the modified eqs. (1) for a number of experimental mixtures of all series and are given in Table IX. Consequently, R being defined as k_{31}/k_{32} , the radical m_3 attacks styrene (M_2) in preference to acrylonitrile (M_1). Yet the values for the relationships k_{31}/k_{32} are rather small when one considers the great difference in the polarity between styrene ($e = -0.8$) and acrylonitrile ($e = +1.20$).

R can also be used in order to examine the validity of the relationship

$$r_{12}r_{23}r_{31} = r_{21}r_{13}r_{32} \quad (2)$$

for the various terpolymers of the present study.^{13,14} As $R = k_{31}/k_{32}$ can also be written $R = r_{32}/r_{31}$, it is possible to calculate the parameter H ,¹⁵

$$H = \frac{r_{12}r_{23}}{r_{21}r_{13}} \cdot \frac{1}{R} \quad (3)$$

which can be defined as measure for the congruity between the theory and the experimental results. For all systems, the value of H is about 0.007, i.e., quite different from the theoretical $H = 1$. Ham¹⁶ reports $H = 0.068$ for the terpolymer styrene-methyl acrylate-vinyl acetate with $r_{31} = 0.01$ and $r_{13} =$

55. Now also in our cases there are two quite extreme r values ($r_{13} = 18$; $r_{12} = 0.04$). Thus, it seems that eq. (3) is not to be applied for such systems, where the values of the reactivity parameters, which express the influence of steric and polar effects, are wide apart.

Wittmer et al.¹⁷ and Ring¹⁸ found that small changes in the values of the reactivity parameters from binary copolymers influence the results of the calculated terpolymer composition. Consequently, the degree of conformity between the experimental and theoretical compositions of terpolymers, eq (1), is an indication for the reliability of the parameters of the binary copolymers and thus confirms the r values obtained for the copolymers of styrene with the various esters and justifies the use of one r value ($r_{13} = 18$) for all acrylonitrile-ester pairs.

The terpolymer eqs. (4),

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]^2 Q_1^2 e^{-e_1^2} + [M_1][M_2] Q_1 Q_2 e^{-e_1 e_2} + \dots + [M_1][M_n] Q_1 Q_n e^{-e_1 e_n}}{[M_1][M_2] Q_1 Q_2 e^{-e_1 e_2} + [M_2]^2 Q_2^2 e^{-e_2^2} + \dots + [M_2][M_n] Q_2 Q_n e^{-e_2 e_n}} \quad (4)$$

$$\frac{d[M_1]}{d[M_n]} = \frac{[M_1]^2 Q_1^2 e^{-e_1^2} + [M_1][M_2] Q_1 Q_2 e^{-e_1 e_2} + \dots + [M_1][M_n] Q_1 Q_n e^{-e_1 e_n}}{[M_1][M_n] Q_1 Q_n e^{-e_1 e_n} + [M_2][M_n] Q_2 Q_n e^{-e_2 e_n} + \dots + [M_n]^2 Q_n^2 e^{-e_n^2}}$$

based on the $Q-e$ scheme are not influenced by the fact¹⁹ that $r_{ij} \simeq 0$. Therefore, it was interesting to examine their applicability for the systems of the present investigation. Using the values for Q and e as reported,² good agreement was obtained for the three systems A-S-MeCC, A-S-BuCC, and A-S-EtHeCC, whereas for the systems A-S-EtCC and A-S-BeCC there are some discrepancies for the m_3 values. Yet these may be due to some inaccuracies of the elemental analyses of nitrogen and oxygen in the terpolymers. For the systems A-S-*c*-HeCC and A-S-*n*-HeCC there is good agreement for the values m_1 and m_2 , but for m_3 the discrepancies are rather wide and not of the magnitude of experimental errors. In order to decide if these were due to the values of e_3 , which were determined by binary copolymerization, the influence of e_3 on the calculated terpolymer compositions was examined by changing its value from 1.50 to 2.60. The calculations showed that e_3 has a strong influence on the value of m_3 , but a rather weak one on m_1 and m_2 . The following calculated average values for e_3 give the best agreement between the experimental and calculated results:

For *n*-HeCC:

$$e_3 = 2.26$$

For *c*-HeCC

$$e_3 = 2.00$$

As shown previously,² in the correlation of the e_2 values of our ester comonomers and the σ^* constants of the various alkyl groups, the points for the *n*-hexyl and the cyclohexyl ester are quite above the line drawn through the other points. The new e_2 values for these two esters are lower, yet they are too low and thus show no linear dependence from σ^* .

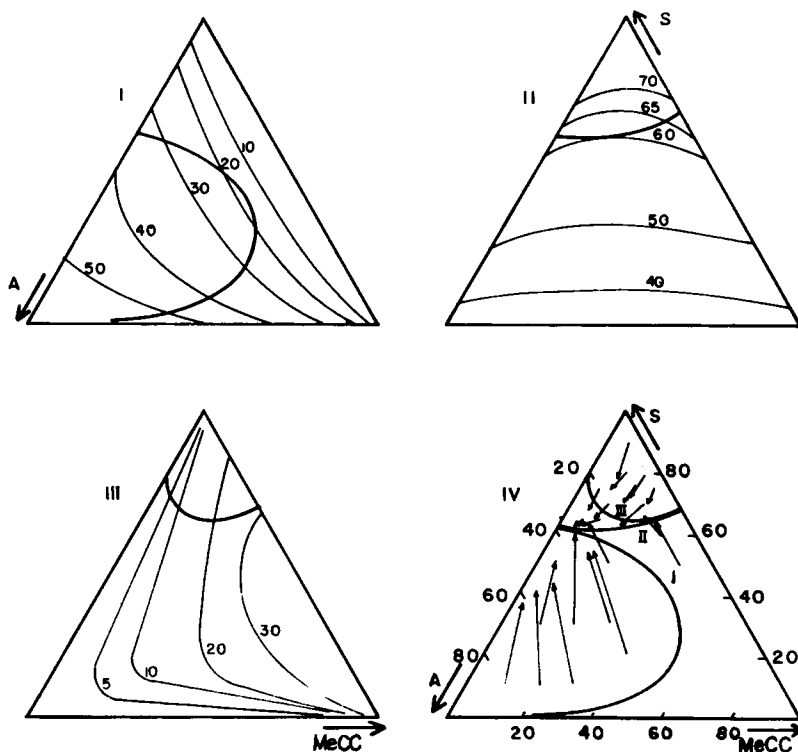


Fig. 9. Contour maps and partial azeotropic lines for acrylonitrile (I), styrene (II), and methyl α -cyanocinnamate (III). Dependence of terpolymer composition on monomer feed on map of partial azeotropic lines (IV).

In order to study the behavior of each monomer during polymerization, O'Driscoll's graphic method²⁰ for determination of azeotropic lines was applied. Taking the terpolymer A—S—MeCC for which the molar terpolymer compositions of 54 different starting mixtures were calculated, the points of equal molar percentage in the starting mixture and in the terpolymer were determined for each monomer. Connecting these azeotropic points (Fig. 9, triangles I, II, and III), a curve was obtained for each monomer, which by extrapolation cuts the sides of the triangle at points, representing the azeotropic composition of the corresponding monomer pair. In triangle IV, the azeotropic lines for the three monomers are depicted together with the arrows, which represent the relationship between the monomer mixture and the terpolymer composition. From these, the following conclusions can be drawn. In the area between the azeotropic line 1 and side A—S of the triangle, the molar percentage of acrylonitrile in the terpolymer is lower than in the starting mixture, whereas for all other parts of the triangle the results are opposite. Regarding styrene, its molar percentage decreases in the area between the line 2 and the apex S, but increases for starting compositions outside this area. Regarding the ester comonomers, there is about the same molar percentage of MeCC in the terpolymer as in the starting mixture of those compositions, which are depicted in the area between the line 3 and side S—MeCC, whereas a decrease of m_3 was found for starting compositions outside this area. No real azeotropic ternary composition was found for any of the inves-

tigated polymers, as the three partial azeotropic lines do not intersect. Yet as already proposed by Slocombe,⁷ there exists an azeotropic line along which clear terpolymers are obtained. This line connects the binary azeotropes of the two pairs A—S and S—MeCC (Fig. 1). Further, near this line there exists good agreement for the relationship $m_i/m_j = M_i/M_j$, which corresponds to Ham's definition for the area of partial azeotropy.²¹

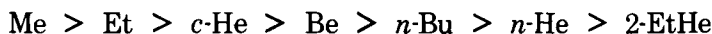
Thermal Behavior of the Terpolymers

Regarding the softening of the various terpolymers, rather wide ranges (20–70°C) were obtained. Now, in order to be able to study the relationship between the softening temperatures and the composition of these terpolymers in spite of the wide ranges, one has to base the comparison on a fixed point. For this purpose, the upper limits of the softening ranges were chosen, as these could be determined quite sharply ($\pm 1^\circ\text{C}$), whereas the beginning is less exact.

Examining the influence of the change of m_3/m_1 at a more or less constant molar proportion of styrene m_2 on the upper softening value for the various terpolymer systems, one can state that there is a rise of the upper value of the softening range with an increase of the proportion m_3/m_1 for the terpolymer systems where m_3 is MeCC, EtCC, or BuCC. In the terpolymers containing BeCC or *c*-HeCC, there exists some rise, whereas for the systems with *n*-HeCC or EtHeCC, no dependence could be found. This different influence of the various ester comonomers m_3 can be explained by a weakening of the intermolecular forces between the polymer chains due to the larger alkyl groups.

The transitions of binary copolymers have been studied extensively, and it is known that there exists a dependence between T_g and the composition of the copolymer, whose influence varies according to its structure and polarity. Regarding the monomers of the present investigation, the T_g 's of the three possible binary systems, i.e., of the copolymers of the various esters of α -cyanocinnamic acid with styrene² and with acrylonitrile,³ and of the copolymer styrene-acrylonitrile²² have been investigated.

For the various terpolymers, there exists a definite dependence of the T_g and the molar proportion of the ester comonomers (m_3), especially in the partial azeotropic region. In Figure 10, one can see a linear relationship between T_g and m_3 and the rise of the glass transition temperature with m_3 increasing up to the values of the binary azeotropes of the ester comonomers with styrene.² At $m_3 = 0$, all the lines converge at about 106°C, the T_g of the azeotropic styrene-acrylonitrile copolymer. Similar to the copolymers with styrene,² the slopes of the glass transition temperatures versus increasing content of the α -cyanocinnamates (m_3) depend on the type of the ester group and decrease in the following order:



fitting the order of increasing size of the ester groups. Thus, the T_g depends on the proportions of polar groups in the terpolymer and on the type of the ester group, which tends to reduce intermolecular interaction and molecular rigidity with increasing size.

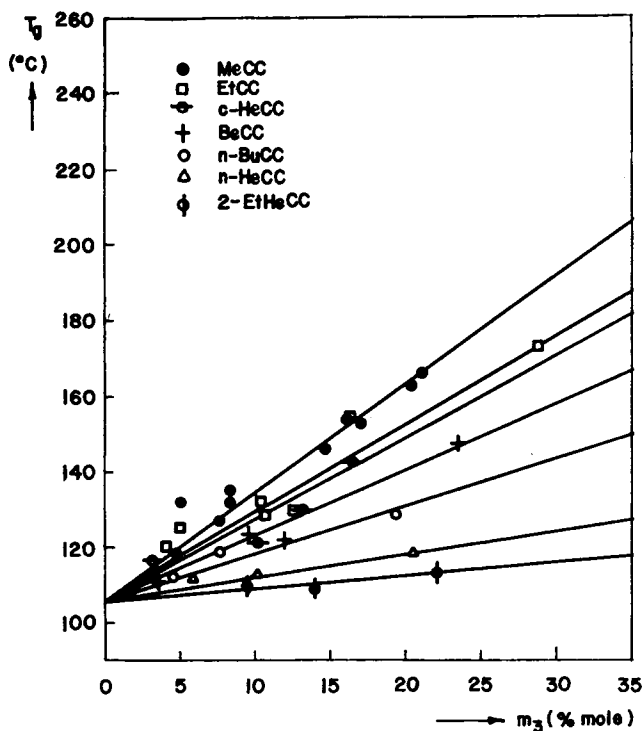


Fig. 10. Dependence of T_g on m_3 for partial azeotropic terpolymers.

TABLE X
Dependence of T_g on m_3

	Ester of α -Cyanocinnamic acid						
	MeCC	EtCC	<i>c</i> -HeCC	BeCC	BuCC	<i>n</i> -HeCC	2-EtHeCC
$\gamma \cdot 10^{-2}$	2.9	2.2	2.0	1.7	1.2	0.5	0.3

As this linear relationship between T_g and m_3 exists at more or less constant proportions of styrene, the influence of change in the proportions m_1/m_2 is rather negligible.

The dependence of T_g on m_3 can be expressed by the equation

$$T_g = T_{gA-S} + \gamma m_3 \quad (5)$$

where m_3 is the molar proportion of α -cyanocinnamate, T_{gA-S} is the glass transition temperature of the copolymer styrene-acrylonitrile at azeotropic proportions (106°C), and γ is a constant, depending on the various types of esters (Table X).

The thermal stability of the terpolymers in dependence of the ester group was studied by thermogravimetric analysis of the various terpolymers of similar molar composition. Considering as start of degradation that temperature, where the weight loss is 5%, $T_{5\%}$ for the different terpolymers was found to be in the range of 300–320°C, i.e., in the range of homopolystyrene. The temperatures where the weight loss reaches 50% are for all terpolymers at about

350°C. The weight loss curves of the terpolymers are quite smooth, being an indication for the homogeneity of the terpolymers against stepwise curves of polymer blends and of blockpolymers.²³

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