

Terpolymerization Studies. II. Terpolymerization of Acrylonitrile, Styrene, and Esters of α -Cyanocinnamic Acid. Polymerization Methods and Properties

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Synopsis

Terpolymers of acrylonitrile, styrene, and seven esters of α -cyanocinnamic acid were prepared by conventional polymerization methods up to high conversions. For emulsion polymerization systems, the rate dependence on the concentration of the emulsifier was determined. Terpolymers, made in suspension and in bulk, were used for the preparation of films and molded specimens in order to study their physical properties/chemical structure relationships.

INTRODUCTION

In part I,¹ the terpolymerization of acrylonitrile, styrene, and a number of esters of α -cyanocinnamic acid was studied and some of the physical properties of the obtained terpolymers were determined.

Now we wish to report details on their preparation in emulsion, suspension, and in bulk and further a study on some of the basic physical and mechanical properties of the various terpolymers in relationship to their chemical structure.

EXPERIMENTAL

Preparation of Monomers and Materials

Acrylonitrile ($A = M_1$), styrene ($S = M_2$), and seven esters of α -cyanocinnamic acid (M_3) were purified or prepared as described in part I.¹ The following esters were used: methyl (MeCC), ethyl (EtCC), *n*-butyl (BuCC), *n*-hexyl (HeCC), cyclohexyl (*c*-HeCC), benzyl (BeCC), and 2-ethylhexyl (EtHeCC) esters.

The initiators, benzoyl peroxide and α,α' -azodiisobutyronitrile (AIBN) were recrystallized from methanol.

Terpolymerization in Emulsion^{2,3}

Polymerizations were carried out in a three-necked flask (250 ml), fitted with stirrer, thermometer, gas-inlet tube, and reflux condenser. The reaction flask was immersed in a water bath with temperature control ($\pm 0.5^\circ\text{C}$). The

TABLE I
 Terpolymerization of A-S-EtCC (33/62/5) in Emulsion.
 Rate Dependence on the Concentration of the Emulsifier.
 Composition of Emulsion Systems at Start^a

	No. 75/1 ^b	No. 75/2	No. 77/1
Water, ml	65	65	65
Emulsifier, gr	0.5	0.25	1

^a Composition of monomer feed: Acrylonitrile (M_1): 0,115 mole (6,10 gr); styrene (M_2): 0,217 mole (22,6 gr); EtCC(M_3): 0,017 mole (3,42 gr). Initiator pair: $K_2S_2O_8$ (0,15 gr); $NaHSO_3$ (0,05 gr). Temperature: $50 \pm 0, 2^\circ C$.

^b Experiment number.

type of stirrer and speed of stirring were identical for all reactions, which were carried out under nitrogen. The emulsifier, sodium lauryl sulfate, was dissolved in demineralized and distilled water in the reaction flask, and the monomer mixture was added at the fixed temperature of polymerization. After stirring for a few minutes, the redox initiator pair, an aqueous solution of potassium persulfate, and then an aqueous solution of sodium bisulfite were added.

The rate of conversion was followed up in the conventional manner by taking samples (1–2 ml) from the reaction flask at various times. At the end of the reaction, the terpolymers were precipitated by adding a saturated aqueous solution of sodium chloride. After filtration and washing of the polymers, first with water and then with methanol, the polymers were further purified by extraction with boiling methanol for about 6 hr. After filtration and drying in the air, the products were dried finally at about $90^\circ C$ under reduced pressure.

Terpolymerizations in emulsion were carried out only for the terpolymer A-S-EtCC, in order to study the kinetics of polymerization as a function of the concentration of the emulsifier (Table I; Fig. 1) and further to follow up the change of composition of the terpolymers with increasing conversion (Table II; Fig. 2).

The compositions of the terpolymers were determined by elemental analysis.

Terpolymerization in Suspension^{4a}

The reactions were carried out in a resin-flask, heated by a thermocontrolled heating-mantle and fitted with a Teflon stirrer, reflux condenser, thermometer, dropping funnel, and gas-inlet tube for nitrogen. Water containing the suspension stabilizer poly(vinyl alcohol) (medium viscosity, du Pont product) was heated to the required temperature. Then the monomer mixture containing the initiator benzoyl peroxide was added quickly through the dropping funnel under constant stirring (about 160 rpm). Later, the temperature was raised to about $90^\circ C$ and kept there for about 2 hr. The terpolymers were obtained in the form of small pearls, which were separated, washed with warm water and with methanol, and then dried at about $60^\circ C$ under reduced pressure.

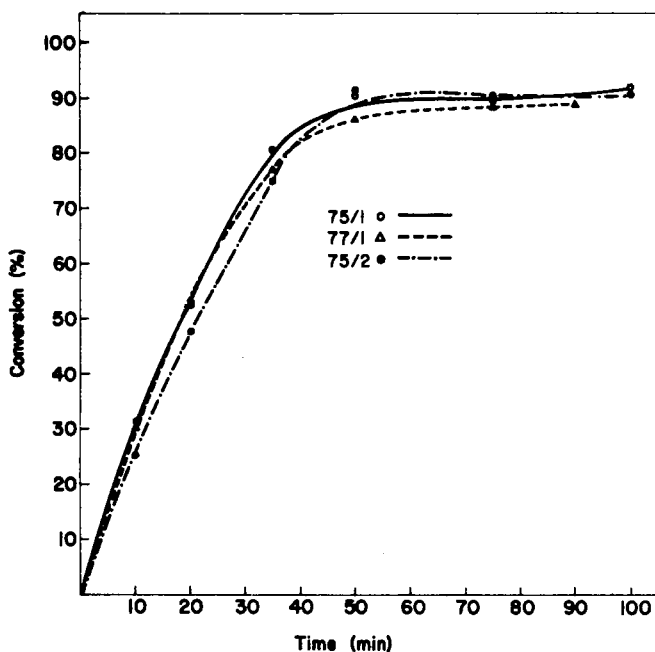


Fig. 1. Terpolymerization of A-S-EtCC in emulsion. Rate dependence on the concentration of the emulsifier.

TABLE II
Terpolymerization of A-S-EtCC in Emulsion. Composition of Terpolymers Versus Degree of Conversion. Composition of Emulsion Systems at Start

Experiment no.	Molar ratio $M_1/M_2/M_3$	Monomer feed						Initiator pair			
		Acrylonitrile (M_1)		Styrene (M_2)		EtCC (M_3)		Water, ml	Emul-sifier, gr	$K_2S_2O_8$, gr	Na- HSO_3 , gr
		gr	mole	gr	mole	gr	mole				
71	33/62/5	12.25	0.231	45.20	0.434	7.03	0.035	185	1.5	0.30	0.10
76.1	33/62/5	6.10	0.115	22.60	0.217	3.42	0.017	90	0.70	0.15	0.05
84.1	20/65/15	3.18	0.060	20.28	0.195	9.04	0.045	65	1	0.15	0.05
84.2	6/69/25	0.95	0.018	21.53	0.207	15.07	0.075	65	1	0.15	0.05

Terpolymerizations in suspension were carried out for all ester comonomers with three different compositions of monomer feed. Details on the conditions and results are summarized in Tables III and IV.

Terpolymerization in Bulk^{4b}

Polymerizations in bulk up to high conversions were carried out in a cell made of two glass plates (about 120 mm/80 mm) separated by Teflon tubing (diameter 1.5–2.5 mm) and held together by several clamps. The monomer mixture containing the initiator AIBN (0.5% by weight of monomers) was prepolymerized in a three-necked flask fitted with a magnetic stirrer, thermometer, reflux condenser, and a gas-inlet tube for nitrogen. After heating the reaction mixture at 80°C in a water bath for 10 min, the viscous mixture was cooled to room temperature and poured into the glass cells. The filled glass cells were put in an oven, and there the polymerization was continued to completion. After cooling, the strong polymer sheets could be separated eas-

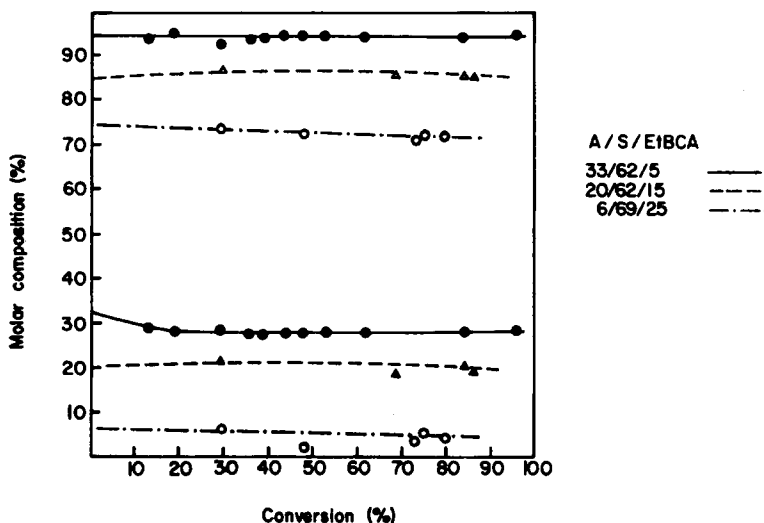


Fig. 2. Terpolymerization of A-S-EtCC in emulsion. Composition vs. conversion.

ily from the glass plates. The glass-clear polymers were either colorless or slightly yellow.

Heating conditions in the oven, T_g values, and results of mechanical tests of the terpolymers are summarized in Table V.

Mechanical Tests

Generally, it should be pointed out that, in order to study the influence of the chemical structure of the terpolymers on their mechanical properties, testing was performed on terpolymer specimens which contained no additives, such as external heat and light stabilizers, lubricants, etc.

All measurements of the mechanical properties of the molded specimens and cast sheets were performed at a room temperature of 25°C and at a relative humidity of 60%. The tests of films were carried out at 27°C and 62% relative humidity.

Tensile Strength

Testing of the tensile strength of films and molded specimens were carried out on an Instron apparatus.

The film strips for testing, 100 mm long and 10 mm wide, were cut from films obtained by casting solutions of the various terpolymers in methyl ethyl ketone on glass plates and evaporating the solvent at about 60°C, first at atmospheric pressure and then at reduced pressure.

Molded specimens, having an ASTM D-638 type form (length, 50 mm; width of constricted part, 8 mm; height, 2.5 mm) were prepared from the terpolymers made by the suspension method by injection molding with a Flogun (Canadian Aviation Electronics Ltd.), whereas rectangular specimens (length, 70 mm; width, 10 mm) were made by cutting from larger moldings or from cast sheets.

TABLE III
Terpolymerization in Suspension

Monomer feed molar ratio $M_1/M_2/M_3$	Monomers						Water, ml	Stabi- lizer, gr	Ini- tiator ^a , %	Temper- ature, °C	Time, hr
	Acrylonitrile (M_1)		Styrene (M_2)		Ester comonomer (M_3)						
	mole	gr	mole	gr	mole	gr					
13.5/70/16.5	0.13	6.9	0.68	70.7	0.16	see Table IV	300	1	0.4	75	3
27/63/10	0.27	14.9	0.63	65.5	0.10	see Table IV	250	1	0.5	95	1-3.5
33/62/5	0.693	37.75	1.302	135.6	0.105	see Table IV	585	2	0.1	90	2
										80	4
										90	1.5-2

^a Per weight of monomer mixture.

TABLE IV
 Terpolymerization in Suspension

Monomer feed molar ratio $M_1/M_2/M_3$	Experi- ment no.	Ester comonomer		Time total, hr	Yield, %	Analysis ^a		Terpolymer			T_g^a °C	$[\eta]^a$ dl/g	Appear- ance ^b
		M_3	gr			N, %	O, %	m_1	m_2	m_3			
13.5/70/16.5	116/1	MeCC	29.6	6.5	75	3.53	4.80	0.114	0.716	0.169	153	0.722	tp
	118/1	EtCC	33.2	5	60	3.26	5.29	0.094	0.679	0.220	155	0.582	tp + tl
	120/1	<i>n</i> -BuCC	37.6	4	87	3.44	4.82	0.110	0.710	0.177	129.5	0.768	tp + tl
	121/1	<i>n</i> -HeCC	42.2	5	91	2.84	4.55	0.075	0.747	0.176	116	0.662	tl
	122/1	<i>c</i> -HeCC	42.0	5	92	3.48	4.13	0.143	0.701	0.155	141	0.516	tp
	123/1	BeCC	43.5	5	86	3.19	4.16	0.119	0.719	0.160	130.5	0.612	tp + tl
	124/1	2-EtHeCC	47.0	5	88	2.74	4.57	0.092	0.747	0.160	110.5	0.658	tp + tl
	125/1	MeCC	18.7	4	86	4.53	3.07	0.227	0.676	0.096	130.5	0.730	tp
	126/1	EtCC	20.1	4	76	4.70	2.85	0.239	0.673	0.086	125	0.718	tl + tp
	127/1	<i>n</i> -BuCC	22.9	4	77	3.81	3.17	0.181	0.714	0.104	119	0.602	tl
	128/1	<i>n</i> -HeCC	25.7	4	77	3.01	2.90	0.111	0.808	0.079	111	0.599	tp
	129/1	<i>c</i> -HeCC	25.5	4	69	3.61	2.34	0.189	0.734	0.075	131	0.538	tl + tp
33/62/5	130/1	BeCC	26.3	4	84	3.28	2.65	0.161	0.749	0.088	124.5	0.570	tl + tp
	131/1	2-EtHeCC	28.5	4	82	3.29	3.04	0.115	0.806	0.078	107	0.540	tl + tp
	90/1	MeCC	19.6	6	75	5.03	1.60	0.288	0.665	0.046	114	1.675	tl
	89/1	EtCC ^c	14.1	6	90	5.04	1.57	0.289	0.665	0.045	113.5	1.565	tl
	91/1	<i>n</i> -BuCC	23.0	5.5	78	4.74	1.63	0.278	0.674	0.048	109	1.515	tl
	92/1	<i>n</i> -HeCC	27.0	5.5	95	4.30	1.61	0.254	0.697	0.049	107.5	1.620	tp
	93/1	<i>c</i> -HeCC	26.8	5.5	65	3.64	1.80	0.208	0.734	0.057	115	1.270	tp
	94/1	BeCC	27.6	5.5	94	4.82	1.69	0.284	0.664	0.050	111	1.465	tp
	95/1	2-EtHeCC	29.9	5.5	95	4.53	1.77	0.268	0.676	0.055	104.5	1.375	tl + tp

^a For purified terpolymer, precipitated twice by methanol from solution in MEK.

^b tl: translucent; tp: transparent.

^c Smaller batch.

TABLE V
Terpolymerization in Bulk^a

Experiment no.	Ester comonomer		Heating conditions in oven, °C (hours)	Terpolymer				Modulus of elasticity, kg/cm ² × 10 ⁻⁴
	M ₁	gr		T _g , crude, °C	Impact strength, ft-lb/in.	Tensile strength, kg/cm ²	Elongation, %	
110/1	MeCC	2.81	50 (21); 80 (48)	95.5	1.02	560	5.2	1.99
111/2	EtCC	3.0	50 (22); 70 (72)	97.5	1.12	515	4.5	2.03
111/3	<i>n</i> -BuCC	3.43	50 (48); 60 (24); 90 (2)	94	0.91	514	5.5	1.26
109/2	<i>n</i> -HeCC	3.25	45 (19); 70 (24); 100 (7)	96	0.71	469	5.3	1.11
111/5	<i>c</i> -HeCC	3.82	50 (22); 70 (72)	89.5	1.09	492	4.2	1.95
111/6	BeCC	3.94	50 (22); 70 (72)	91	1.04	537	4.0	1.70
111/7	2-EtHeCC	4.27	50 (48); 60 (24); 90 (2)	89	1.12	430	5.5	1.68
115/1	polystyrene		50 (72); 80 (2)	89	0.78			
115/2	azeotropic A-S		50 (71); 80 (2)	84	1.08			

^a Monomer feed molar ratio: M₁/M₂/M₃ = 33.2/62.5/4.3. Composition of monomer feed: acrylonitrile (M₁), 0.116 mole (6.15 g); styrene (M₂), 0.217 mole (22.55 g); ester comonomer (M₃), 0.015 mole.

Impact Strength

The impact strength of the terpolymers was tested on a Hounsfield Plastic Impact Testing Machine using rectangular specimens (length, 45 mm; width, 6 mm; height, about 1.5 mm) without notch.

DISCUSSION

Emulsion Polymerization

Terpolymerizations in emulsion up to high conversions were carried out only with the system A-S-EtCC at partial azeotropic composition. All the terpolymers were soluble in methyl ethyl ketone, and no homopolyacrylonitrile was obtained, although this occurs frequently with copolymerizations of acrylonitrile in emulsion, due to the partial solubility of acrylonitrile in water.² Similar to the copolymerization of styrene with EtCC,³ the terpolymer A-S-EtCC was obtained in high yield at a nearly constant rate up to conversions of 85–90%.

Regarding the influence of the emulsifier on the rate of polymerization, no differences were found at the three concentrations tested (Fig. 1).

Using three different starting mixtures, the changes of composition during conversions up to about 90% are rather small (Fig. 2). In all the three compositions, the styrene content remains nearly constant, as was to be expected due to the presence of the azeotropic line for styrene⁵ and the system A-S-EtCC = 20/65/15 shows actually azeotropic conduct during the whole range of conversion. The starting mixture A-S-EtCC = 33/62/5 behaves like an azeotrope above 20% conversion, while in the first stages of polymerization, the acrylonitrile content in the terpolymer is somewhat lower than in the feed. This could be attributed to the dissolution of some of the acrylonitrile in water. For composition A-S-EtCC = 6/69/25, there is a slight yet steady decrease of the ratio m₁/m₃ with increasing conversion. Thus, at the region near the binary azeotrope A-S, a more or less homogeneous terpolymer can be obtained even up to nearly quantitative conversion.

Suspension Polymerization

Partial azeotropic terpolymers were prepared by the suspension method in good yields. Some of the terpolymers were obtained as transparent pearls, which dissolved completely in methyl ethyl ketone, whereas some terpolymers contained translucent pearls, which left a small residue after dissolving them in methyl ethyl ketone. These residues were soluble in dimethylsulfoxide and, as determined by IR spectroscopy, had a higher acrylonitrile content and a lower ester content than the corresponding terpolymer.

The intrinsic viscosity of all terpolymer systems was determined for three different compositions in the partial azeotropic region. The results show (Fig. 3) that, with the increase of the ratio m_3/m_1 from about 0.15 up to 0.5–0.7, the intrinsic viscosity is decreasing sharply, but remains then fairly constant at higher ratios.

The terpolymers, prepared in suspension, contained some residual monomers or very low molecular weight polymers (1–4%). Comparison of the T_g of a purified terpolymer (obtained by precipitation from its solution in methyl ethyl ketone) with the T_g of the crude polymer indicates that the latter is reduced by about 4°C for each per cent of monomer present.

Homogeneous, colorless, transparent films were prepared from cast solutions of the various suspension terpolymers by evaporation of the solvent. Regarding their tensile strength (Table VI), the maximum values for all types were obtained for terpolymer films made from a starting composition of $M_1/M_2/M_3 = 33/62/5$, when the terpolymer film A-S-c-HeCC shows the highest value. An increase of the ratio M_3/M_1 and consequently of m_3/m_1 results in a decrease of the tensile strength. Yet all the films were rather brittle and their elongations were 2–3%. Thus, the bulky ester groups, even at about 15 mole-%, have not enough plasticizing power to counteract the brittleness of the polymers due to the styrene moieties and the intermolecular forces from the polar nitrile groups.

Transparent molded specimens were prepared by injection molding. There was no difficulty to mold by injection the terpolymers with an ester content of about 5 mole-%, but it was rather difficult to mold specimens from

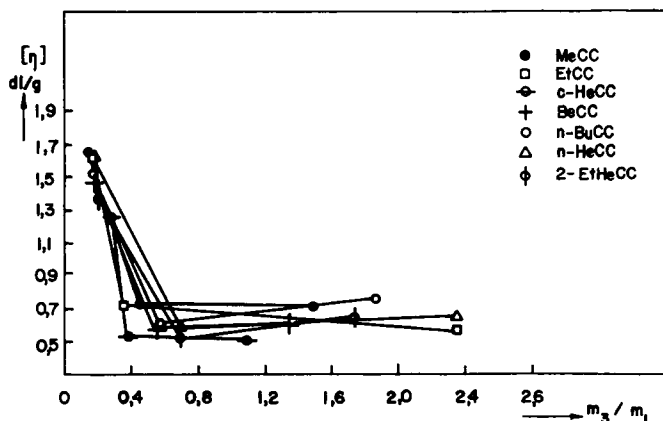


Fig. 3. Terpolymerization in suspension. Dependence of $[\eta]$ on the ratio m_3/m_1 , of partial azeotropic terpolymers.

TABLE VI
 Terpolymerization in Suspension. Tensile Properties of Films and of Injection Molded Specimens

Experi- ment no.	Ester comonomer M ₃	Terpolymers mole fraction			Films			Molded specimens		
		m ₁	m ₂	m ₃	Tensile strength, kg/cm ²	Elonga- tion max., %	Modulus of elasticity, ^a kg/cm ² × 10 ⁻⁴	Tensile strength, kg/cm ²	Elonga- tion max., %	Modulus of elasticity ^b kg/cm ² × 10 ⁻⁴
90/1	MeCC	0.288	0.665	0.046	445	2.4	2.12	545	6.5	1.46
125/1	MeCC	0.227	0.676	0.096	449	2.6	1.77	243	2.3	1.10
116/1	MeCC	0.114	0.716	0.169	298	1.7	1.97	246	2.0	0.96
89/1	EtCC	0.289	0.665	0.045	390	2.6	1.75	425	3.0	1.35
126/1	EtCC	0.239	0.673	0.086	289	2.5	1.31	195	2.0	1.09
118/1	EtCC	0.094	0.679	0.220	283	1.8	1.69	—	—	—
91/1	<i>n</i> -BuCC	0.278	0.674	0.048	428	2.8	2.11	460	3.8	1.42
127/1	<i>n</i> -BuCC	0.181	0.714	0.104	322	2.0	1.75	273	1.3	1.0
120/1	<i>n</i> -BuCC	0.110	0.710	0.177	351	2.8	1.48	180	1.6	1.22
92/1	<i>n</i> -HeCC	0.254	0.697	0.049	439	2.9	2.12	595	5.7	1.41
128/1	<i>n</i> -HeCC	0.111	0.808	0.079	208	2.4	1.18	141	1.3	1.09
121/1	<i>n</i> -HeCC	0.075	0.747	0.176	143	1.1	1.36	133	1.3	1.11
93/1	<i>c</i> -HeCC	0.208	0.734	0.057	514	3.4	2.03	565	5.5	1.39
129/1	<i>c</i> -HeCC	0.189	0.734	0.075	204	1.4	1.82	141	1.5	1.06
122/1	<i>c</i> -HeCC	0.143	0.701	0.155	183	1.5	1.50	—	—	—
94/1	BeCC	0.284	0.664	0.050	463	2.8	2.21	645	5.8	1.46
130/1	BeCC	0.161	0.749	0.088	304	1.9	1.19	150	2.0	0.98
123/1	BeCC	0.119	0.719	0.160	77	0.8	1.47	—	—	—
95/1	2-EtHeCC	0.268	0.676	0.055	430	2.8	2.78	555	6.1	1.35
131/1	2-EtHeCC	0.115	0.806	0.078	182	1.2	1.37	170	1.0	1.05
124/1	2-EtHeCC	0.092	0.747	0.160	150	1.1	1.41	—	—	—

^a From tensile strength. Initial width of grips, 20 mm; speed of testing, 5 mm/min.

^b From tensile strength. Initial width of grips, 15 mm; speed of testing, 2 mm/min.

terpolymers which, due to a higher ester content, had a higher melting range. Similarly to the films, the tensile properties of terpolymers of the partial azeotropic region—at a more or less constant molar percentage of styrene—depend also on the ratio of m_3/m_1 , yet there is no clear relationship with the various ester groups (Table VI).

Thus, the values for the tensile strength and maximal elongation of the different terpolymers with an ester content of about 5 mole-% are similar to those of commercial polystyrene or styrene-acrylonitrile copolymer, whereas their moduli of elasticity are lower.⁶ An increase of the ester content (m_3) up to about 10 mole-% has little influence on the moduli of elasticity, but causes a sharp decrease of the tensile strength and of the elongation. This may be due to some degradation which occurs during the molding operation, when higher molding temperatures are necessary for terpolymers with increasing m_3/m_1 ratios because of the corresponding increase of their T_g .

Bulk Polymerization

Transparent and colorless terpolymer sheets were prepared by bulk polymerization at the partial azeotropic region, containing about 5 mole-% of the various ester comonomers (m_3). This method is commercially used for the production of acrylic sheets and seems quite useful for these terpolymers. The influence of the various ester comonomers on the mechanical properties of these cast terpolymer sheets was studied. Even at such a low percentage of the comonomer m_3 , one can observe a dependence of the tensile strength on the ester type. Thus, the tensile strength decreases with increasing length of the alkyl group in the ester: $\text{Me} > \text{Et} \approx n\text{-Bu} > n\text{-He} > 2\text{-EtHe}$, while the *c*-HeCC and BeCC containing terpolymers are quite similar to the EtCC terpolymer. Generally, the values of the tensile strength of the bulk specimens are of the same magnitude as the values of those made by injection molding. The dependence of the maximal elongation and the modulus of elasticity on the various ester groups is not apparent.

Regarding the impact strength, this property is quite sensitive to the molecular weight, chain structure, etc., of the polymer, and also to the method of preparation of the specimens. Consequently, cast sheets of polystyrene and of the azeotropic copolymer acrylonitrile-styrene, prepared at identical conditions as the terpolymers, were used for comparative tests. The terpolymers, except the one containing *n*-HeCC, show a higher impact strength than polystyrene and are about equal to the copolymer acrylonitrile-styrene. Yet the fact should be stressed that the upper "use" temperatures of these terpolymers are 5° to 15°C higher than those of polystyrene or the acrylonitrile-styrene copolymer.

Summarizing, it can be stated that, whereas the investigated physical and mechanical properties of these styrene-rich terpolymers are influenced mainly by the ester comonomers and to a lesser extent by the acrylonitrile, no striking effect due to any one of the ester groups could be recorded.

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