

Terpolymerization Studies: IV. Terpolymerization of Ethyl Acrylate, Ethyl α -Cyanocinnamate, and Styrene

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SYNOPSIS

Ethyl acrylate, ethyl α -cyanocinnamate, and styrene were terpolymerized by free radical initiation at 60°C up to low conversion. The relationships between monomer feed and compositions of the terpolymers were determined by a triangular graph according to Slocombe. The terpolymers were characterized by their IR and Proton NMR spectra, intrinsic viscosity, and thermal behaviour. For a selected terpolymer, its adhesive properties for a number of substrates was investigated.

INTRODUCTION

In the recently reported syntheses of the copolymers of ethyl α -cyanocinnamate (ECC) with three esters of acrylic acid, ECC reacted rather reluctantly with these acrylates.¹ A maximal ECC content of about 13 mol % in the copolymers was obtained only with a great excess of ECC in the starting mixture, but it had little influence on the thermal properties in comparison with the acrylate homopolymers. In addition, the adhesive properties of the copolymers were rather weak.

In an attempt to improve these properties, styrene was added to the system ethyl acrylate–ECC as third monomer with the objective to synthesize the corresponding terpolymer.

EXPERIMENTAL

Materials and Preparation of Monomers

Ethyl acrylate, Fluka product, was distilled at 45°C/110 mm Hg and styrene, Fluka product, was purified by washing with aqueous sodium hydroxide, drying

and distilling at 60–61°C/45 mm Hg. Ethyl α -cyanocinnamate was prepared as described before.² Benzoyl peroxide was recrystallized from methanol.

Terpolymerization

Terpolymerizations were carried out in bulk up to low conversion at $60 \pm 0.5^\circ\text{C}$ in sealed glass tubes as described before,¹ using benzoyl peroxide (0.2% weight) as free radical initiator. The total monomer feed was 5.0 g. For determination of the compositions of the terpolymers and of some of their physical properties, the reaction tubes were cooled, opened, and the various terpolymers precipitated in methanol at predetermined times, i.e., at less than 10% conversion. The products were purified by reprecipitation from methyl ethyl ketone solution by methanol. The terpolymers, after drying at about 60°C/0.1 mm Hg, were obtained as white powders. Their composition was determined by elementary analysis of their nitrogen and oxygen content. Details on the conditions of the terpolymerizations and the results are summarized in Table I.

The relationship between the molar composition of the obtained terpolymers and the corresponding monomer feed is given by Slocombe's triangle method³ in Figure 1, as described before.⁴

Physical Test Methods

The terpolymers were characterized by IR and NMR spectroscopy, intrinsic viscosity, and solubility as

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Table I Terpolymerization of Ethyl Acrylate (M_1), Ethyl α -Cyanocinnamate (M_2) and Styrene (M_3) in Bulk

Exp. No.	Monomer Feed Mole Fraction			Time of Reaction (min)	Conversion (%)	Terpolymer							
	M_1	M_2	M_3			N (%)	O (%)	Mole Fraction			$[\eta]$ (dL/g)	Melting Range ($^{\circ}$ C)	T_g ($^{\circ}$ C)
								m_1	m_2	m_3			
30	0.9	0.05	0.05	75	2.9	0.49	25.03	0.783	0.037	0.183	—	195–210	—
10	0.8	0.1	0.1	110	4.0	0.90	19.75	0.600	0.070	0.330	1.015	195–210	51
33	0.7	0.2	0.1	110	3.8	2.70	17.18	0.433	0.243	0.324	0.95	200–210	75
11	0.7	0.1	0.2	90	1.3	0.88	15.67	0.465	0.068	0.467	—	205–215	—
9	0.6	0.2	0.2	90	2.9	1.73	13.37	0.343	0.144	0.513	—	215–225	99
31	0.6	0.1	0.3	110	4.4	1.29	14.02	0.389	0.104	0.507	0.92	200–210	85
32	0.5	0.1	0.4	115	3.2	1.69	12.70	0.322	0.140	0.538	0.90	200–215	95
45	0.2	0.3	0.5	107	4.3	2.87	9.23	0.108	0.265	0.627	—	235–245	—
43	0.2	0.1	0.7	124	4.6	1.69	7.51	0.133	0.142	0.725	0.82	215–225	132
52	0.15	0.25	0.6	110	5.1	2.75	8.63	0.094	0.252	0.654	—	230–245	—
51	0.15	0.15	0.7	105	4.2	2.18	8.00	0.115	0.190	0.695	—	230–245	—
53	0.1	0.25	0.65	100	4.4	2.81	7.88	0.059	0.259	0.682	—	240–250	—
44	0.1	0.2	0.7	117	5.5	2.63	7.70	0.067	0.238	0.695	0.84	240–250	142

described before.¹ The glass transition temperature was determined on a Du Pont Instruments 910 Differential Scanning Calorimeter.

The adhesive strength of the terpolymers and of two related copolymers¹ was determined for various substrates by the tensile lap shear test and the T-Peel test. For these tests, sheets and flexible strips of various substrates were first cleaned in the appropriate way and then covered by a thin layer of a toluene solution (60–70% solids) of the polymer. The solvent was allowed to evaporate for a few min-

utes and then the substrates were pressed together at room temperature.

Tensile Lap Shear Test⁵

Multiples for five test specimens of the sheets of various substrates were made at a pressure of 1 kg/cm² for 3 d. The size of the cut specimens was 4/1" (101.6/25.4 mm) with an overlap of the glued surface of 0.5/1" (12.7/25.4 mm).

T-Peel Test⁶

Multiples for five test specimens of various adherends were prepared at a pressure of 0.2 kg/cm² for 3 d. The size of the cut specimens was 12/1" (304.8/25.4 mm) with a bonded surface of 9/1" (228.6/25.4 mm).

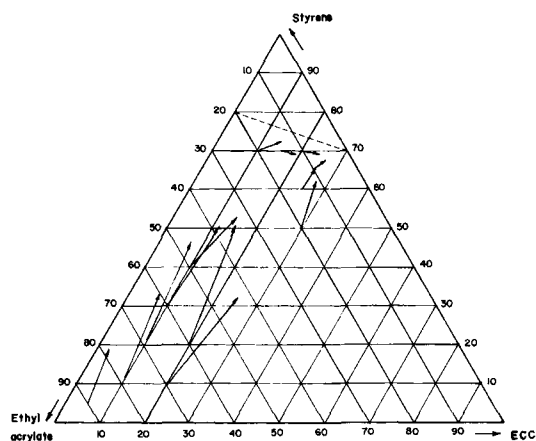


Figure 1 Monomer-terpolymer triangular composition plots for the system ethyl acrylate-ethyl α -cyanocinnamate-styrene.

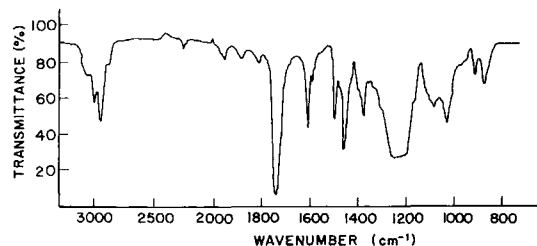


Figure 2 Infrared spectrum of terpolymer ethyl acrylate-ethyl α -cyanocinnamate-styrene (experiment no. 44).

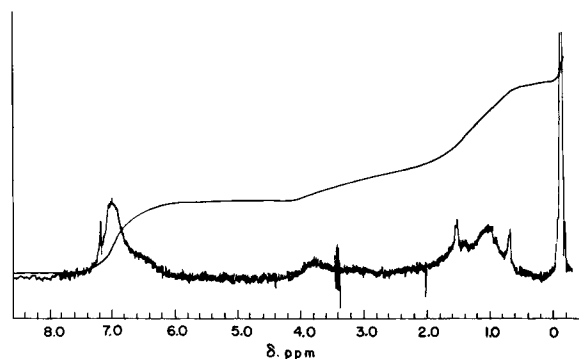


Figure 3 Proton NMR spectrum of terpolymer ethyl acrylate-ethyl α -cyanocinnamate-styrene (experiment no. 44).

RESULTS AND DISCUSSION

Examining the triangle (Fig. 1), one can observe that most of the arrows, whose heads indicate the terpolymer composition obtained from a monomer feed as indicated by their tails, point toward a line that connects the binary azeotropic compositions of the pairs ECC–styrene (0.3/0.7)² and ethyl acrylate–styrene (0.2/0.8).⁷ Slocombe³ designated this line as the azeotropic line. One notices that the arrows are more inclined toward the azeotropic composition of the pair ECC–styrene and also that the arrows get shorter when situated near the azeotropic line, indicating that the composition of terpolymers obtained from monomer feeds of $M_1/M_2/M_3 = 0.1/$

0.2/0.7 (Exp. no. 44) and 0.1/0.25/0.65 (Exp. no. 53), respectively, approximate a ternary azeotropic composition.

Characterization

IR and Proton NMR Spectra

The IR spectra of the terpolymers poly (ethyl acrylate-co-ECC-co-styrene) (Figure 2), as for the copolymers of the acrylates with ECC,¹ have the strong carbonyl ester bands at 1740 cm^{-1} and at $1180\text{--}1260\text{ cm}^{-1}$ (C–O stretching) from the acrylate and ECC. The presence of ECC is confirmed by the nitrile band at 2250 cm^{-1} and the bands of the aromatic ring are at 1600 , 1580 , and 1500 cm^{-1} . The bands of the methylene and methyl groups are at 1460 and 1370 cm^{-1} , respectively.

The proton NMR spectra of the terpolymers were obtained in CDCl_3 solution with TMS (Figure 3). The absorptions are assigned: at about 7.1 ppm to the phenyl ring from styrene and ECC, those at about 4.0 ppm and 1.2 ppm to the methylene and methyl group respectively from the ethyl esters, and those at 1.5–2.2 ppm to the methylene and methine protons of the chain.⁸

Thermal Behaviour

Regarding the glass transition temperature, there is a steady rise with increasing styrene and styrene plus ECC contents, thus showing the strong influ-

Table II Adhesive Strength of Polymers

Polymer ^a	Tensile Shear Strength (MPa)			T-Peel Strength (N/mm)	
	Aluminium–Aluminium	FRP–FRP ^b	Perspex–Perspex	Aluminium–Aluminium	Rubber–Aluminium
Copolymer EA/ECC ^c : 0.9/0.1 exp. no. 57 ¹	1.10	Not tested	Not tested	0.50	1.02
Copolymer EA/ECC ^c : 0.97/0.03 exp. no. 56 ¹	1.22	1.07	1.12	0.12	0.86
Copolymer MA/ECC ^d : 0.9/0.1 exp. no. 59 ¹	0.70	Not tested	Not tested	0.62	0.57
Copolymer MA/ECC ^d : 0.94/0.06 exp. no. 58 ¹	0.91	0.81	0.92	0.66	0.39
Terpolymer EA/ECC/St ^e : 0.07/0.24/0.69 exp. no. 44 (this paper)	3.18	2.50	3.00	Low adhesion	Low adhesion

^a Composition of copolymers is given in molar ratios of the monomers.

^b Fiber-reinforced epoxy resin.

^c EA/ECC, Copolymer ethyl acrylate-ethyl α -cyanocinnamate.¹

^d MA/ECC, Copolymer methyl acrylate-ethyl α -cyanocinnamate.¹

^e EA/ECC/St, Terpolymer ethyl acrylate-ethyl α -cyanocinnamate-styrene.

ence of styrene on the T_g in comparison to the rather low T_g of the copolymer ethyl acrylate-ECC.¹ Indeed, also the values of the intrinsic viscosities of the terpolymers are quite higher than those of the ethyl acrylate-ECC copolymers.¹

Solubility

All terpolymers of this series are soluble at room temperature in chloroform, methyl ethyl ketone, and in toluene, but are insoluble in hexane and methanol.

Bonding Properties

Considering the possible application of the copolymers of ECC with some ester acrylates¹ and of the terpolymers from this paper as thermoplastic adhesives, their bonding performance was evaluated for a number of substrates—aluminum, F.R.P., Perspex, and rubber—by the T-Peel test⁶ and by the Tensile Lap Shear test⁵ (Table II). Thus, the peel strength of aluminum and rubber, bonded with the acrylic copolymers, is quite similar to the peel strength of pressure-sensitive acrylic adhesives used as foil tapes⁹; however, it is only about half of the peel strength of some commercial acrylic adhesives like Flexon 246 and Bostik 896.¹⁰ The terpolymer failed in this series. The values of the shear strength of the acrylic copolymers are rather low and are like those of some silicone adhesives,¹¹ whereas the shear

strength of the terpolymer shows a magnitude quite near that of commercial acrylic adhesives.¹⁰

In general, the adhesive properties of the tested acrylic polymers have to be improved to obtain products for practical applications.

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