Copolymerization of Acrylic Esters with Ethyl α-Cyanocinnamate*

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Synopsis

The copolymers of ethyl α-cyanocinnamate with methyl, ethyl, and butyl acrylate were prepared in toluene solution with benzoyl peroxide as initiator. The copolymerization parameters were determined and the Alfrey–Price Q and e values were calculated. The influence of the comonomer on some of the basic properties of the copolymers, like intrinsic viscosity, solubility, and glass transition temperature, was studied in comparison with the corresponding homopolyacrylates.

INTRODUCTION

Acrylic esters polymerize rather easily by conventional polymerization processes. The bulk polymerization of acrylic esters is characterized by a rapid rate of polymerization and crosslinking occurs already in the early stages of polymerization; thus insoluble gel-like polymers are formed with little practical use.[1] In contrast, their polymerization in solution is easier to control and the resulting polyacrylate solutions are widely used as adhesives and as impregnating materials in paper and textile industries.[2]

Continuing our work on the copolymerization of trisubstituted ethylenes[3–5] and in order to study their influence for various polymeric systems, we wish to report now the free radical initiated copolymerization of ethyl α-cyanocinnamate
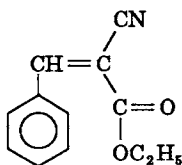
with methyl, ethyl, and butyl acrylate in toluene solution. The copolymerization parameters of the three systems were determined and the Alfrey–Price Q and e values were calculated. The new copolymers were characterized by their main physical properties—intrinsic viscosity, solubility, and glass transition temperature.

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EXPERIMENTAL

Materials and preparation of monomers:

Methyl acrylate: Commercial Fluka product was distilled at 80°C.
Ethyl acrylate: Commercial Fluka product was distilled at 45°C/110 mm Hg.
Butyl acrylate: Commercial Fluka product was distilled at 50°C/20 mm Hg.
Ethyl α-cyanocinnamate (ECC) was prepared as described previously.[3]
Benzoyl peroxide: Eastman pure grade was used after recrystallization from methanol.

Copolymerization

Small-Scale Experiments

All copolymerization experiments of the acrylic esters with ECC for kinetic measurements were carried out in sealed Pyrex tubes with a bulb at the lower end and a constriction near the upper end. The solutions (5 mL) of the monomers in toluene ($M_1 + M_2 = 5$ mol/L) and the initiator (benzoyl peroxide: 0.2% by weight), after introduction into the reaction tubes, were frozen and the tubes were degassed under reduced pressure, flushed twice with nitrogen, evacuated to about 0.1 mm Hg and sealed off. Copolymerizations were performed in a thermostat (at 70 ± 0.5°C) fitted with a shaking device. The reactions were stopped at low conversion, i.e., at less than 10% as determined by trial and error. At the proper time, the tubes were cooled and opened and the content was poured into a suitable precipitant for the copolymer. The product copolymers were purified by successive reprecipitation from their solution in methyl ethyl ketone (MEK) and were then dried at 50°C under reduced pressure to constant weight.

"Large-Scale" Experiments

In order to obtain larger quantities of the copolymers for investigating their adhesive strength, several copolymers were prepared on larger scale (100 mL solution) to higher conversions according to the method of Hanna.[6] The reactions were carried out in a three-necked flask, placed in a temperature-controlled bath (70 ± 0.5°C), and fitted with a mechanical stirrer, gas inlet tube for nitrogen, a graduated funnel for subsequent additions of the ester acrylates, and reflux condenser with a trap to prevent the entrance of air. The copolymers were precipitated and purified in the manner of the small-scale experiments.

All the copolymers were obtained as translucent yellowish rubbery solids. Their composition was determined by elemental microanalyses of their nitrogen content. Details on reaction conditions, results, and properties of the copolymers are summarized in Tables I, II, and III.

Physical Test Methods

Spectroscopic Measurements

Infrared spectra (IR) of solutions of the copolymers in chloroform or in admixture with KBr were carried out on a Perkin-Elmer 237 grating IR spec-

TABLE I
Copolymerization of Methyl Acrylate and Ethyl α-Cyanocinnamate in Solution[a]

Experiment no.	Monomer feed mole fraction		Time (min)	Conversion (%)	Elemental analysis (N%)	Copolymer Mole fraction		η (dL/g)	T_g (°C)
	M_1	M_2				m_1	m_2		
				Low conversion					
39	1.0	0	5	6.9	—	1.0	—	1.00	11[b]
34	0.9	0.1	27	11.8	0.12	0.9925	0.0075	0.77	—
35	0.75	0.25	55	8.1	0.37	0.977	0.023	0.44	—
42	0.6	0.4	55	4.0	0.73	0.952	0.048	0.33	2.5
28	0.5	0.5	168	9.8	1.09	0.926	0.074	0.30	11
8	0.4	0.6	210	3.9	1.23	0.916	0.084	—	11
29	0.3	0.7	225	2.8	1.79	0.871	0.129	—	—
				High conversion					
58	0.75	0.25	300	46.2	—	0.94[c]	0.06[c]	0.43	—
59	0.4	0.6	360	15.9	—	0.9[c]	0.1[c]	0.24	—

[a] Precipitant: hexane.
[b] Shetter[7] reports 8°C.
[c] From NMR spectrum.

TABLE II
Copolymerization of Ethyl Acrylate and Ethyl α-Cyanocinnamate in Solution[a]

Experiment no.	Monomer feed mole fraction		Time (min)	Conversion (%)	Elemental analysis (N%)	Copolymer Mole fraction		η (dL/g)	T_g (°C)
	M_1	M_2				m_1	m_2		
				Low conversion					
38	1.0	—	5	14.3	—	1.0	—	1.62	−23[b]
36	0.9	0.1	18	9.3	0.14	0.990	0.010	—	−31
37	0.75	0.25	53	8.3	0.39	0.971	0.029	0.53	−23
17	0.6	0.4	145	6.8	1.04	0.920	0.080	—	−31
16	0.5	0.5	65	3.2	1.07	0.918	0.082	0.38	−17
7	0.4	0.6	205	3.7	1.10	0.915	0.085	—	—
15	0.3	0.7	254	7.4	1.66	0.865	0.135	0.27	−23
				High conversion					
56	0.75	0.25	300	38.8	0.45	0.967	0.033	0.50	—
57	0.4	0.6	390	13.9	1.31	0.897	0.103	0.29	—

[a] Precipitant: hexane.
[b] Shetter[7] reports −24°C.

Experiment no.	Monomer feed mole fraction		Time (min)	Conversion (%)	Elemental analysis (N%)	Copolymer Mole fraction		η (dL/g)	T_g (°C)
	M_1	M_2				m_1	m_2		
40	1.0	—	5	15.9	—	1.0	—	2.2	−55[b]
24	0.75	0.25	40	7.6	0.36	0.966	0.034	0.70	−55
23	0.6	0.4	60	4.9	0.60	0.943	0.057	0.57	−50
26	0.5	0.5	175	10.0	1.10	0.893	0.107	0.49	−36
27	0.3	0.7	225	3.9	1.38	0.864	0.136	—	−31

[a] Precipitant: methanol.
[b] Shetter[7] reports −54°C.

trometer. Proton NMR spectra of the copolymers in solutions of $CDCl_3$ with tetramethylsilane as internal standard were performed on a Varian T-60 spectrometer.

Viscosity

The intrinsic viscosity of the various copolymers was determined from viscosity measurements of their solutions in MEK with an Ubbelohde viscometer at $30 \pm 0.1°C$ (Tables I, II, and III).

Glass Transition Temperature

T_g of the copolymers was determined on a BDL micro differential thermal analyzer, Model M-3, at a heating rate of 5°C/min. Before starting the test, the samples and the reference (quartz) were frozen in liquid air (Tables I, II, and III).

RESULTS AND DISCUSSION

The copolymerization parameters r_1 and r_2 of the three systems of ethyl α-cyanocinnamate with methyl, ethyl, and butyl acrylate were determined from low-conversion experiments by the Kelen and Tüdös graphical method[8] (Figs. 1–3) according to the equation

$$\eta = r_1\xi - (r_2/\alpha)(1 - \xi) \tag{1}$$

where $\eta = x(y - 1)/(\alpha y + x^2)$ and $\xi = x^2/(\alpha y + x^2)$, x denotes the ratio of the mole fractions of the two monomers in the feed, and y is the ratio of their mole fractions in the copolymer. The parameter α is given by $\alpha = \sqrt{F_m \cdot F_M}$, where F_m and F_M stand for the lowest and highest x^2/y value, respectively.

The values of r_1 of the three systems are of the same magnitude (Table IV), showing a slight decrease with increasing chain length of the alkyl group. As
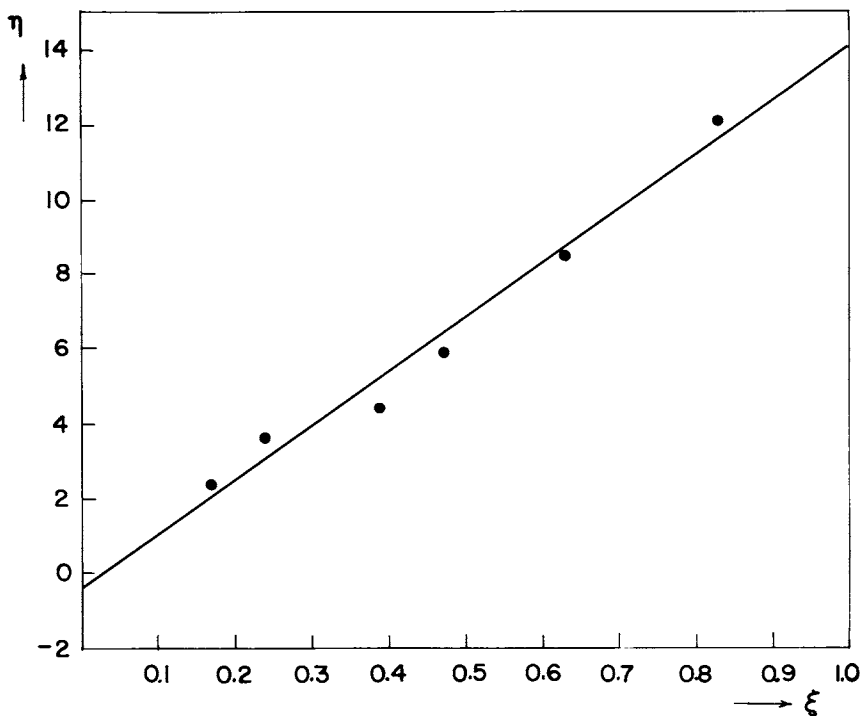
Fig. 1.   Copolymerization of methyl acrylate (M_1) with ECC (M_2). Determination of reactivity ratio by the Kelen and Tüdös method.
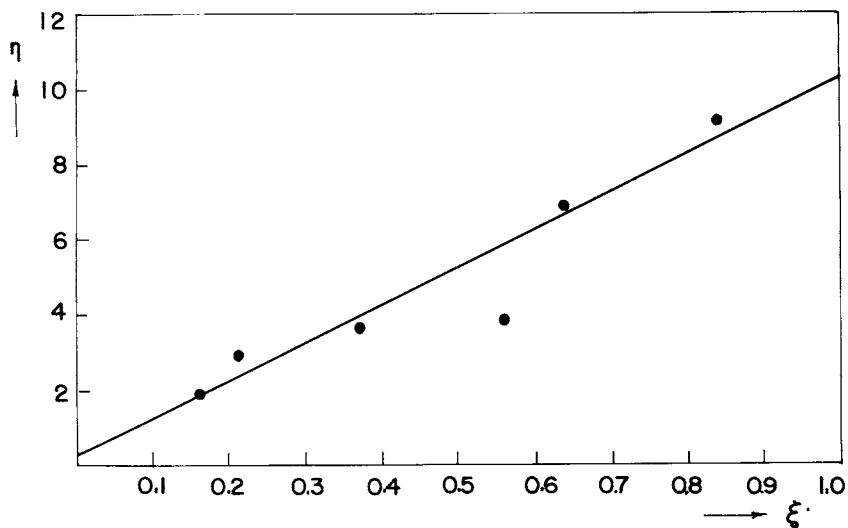

Fig. 2.   Copolymerization of ethyl acrylate (M_1) with ECC (M_2). Determination of reactivity ratio by the Kelen and Tüdös method.
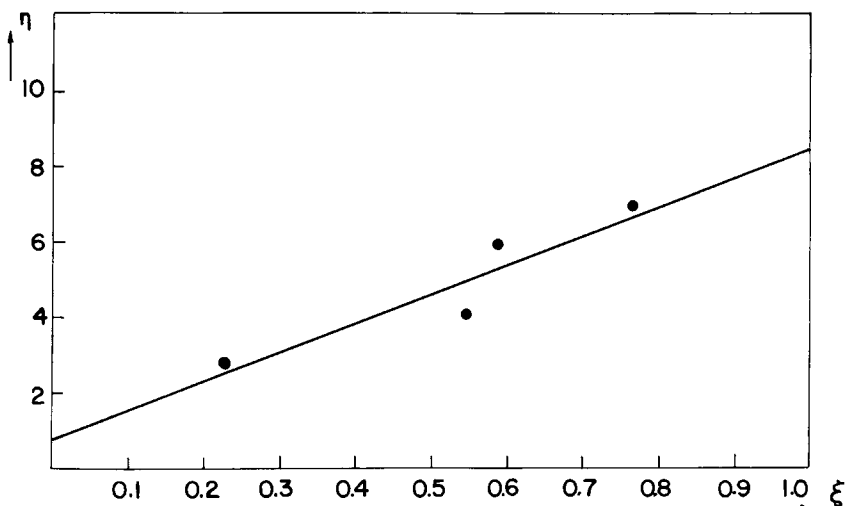
Fig. 3. Copolymerization of butyl acrylate (M_1) with ECC (M_2). Determination of reactivity ratio by the Kelen and Tüdös method.

already reported previously,[3] the comonomer does not homopolymerize at the given conditions and thus $r_2 = 0$. The low and even negative values for r_2 are to be ascribed to some inaccuracies in the elemental analyses.[4] Like for the copolymer ECC–acrylonitrile,[4] there seems to be no penultimate effect for the three ECC–acrylate copolymers, when examined by the scheme of Merz et al.[9] and the notation of Barb.[10]

The copolymer composition curves in dependence of the monomer charges are quite similar for the three systems and all show a much higher acrylate content in the product copolymer than in the starting mixture (Fig. 4). Notwithstanding these differences between the compositions of the copolymers vs. that of the corresponding monomer feed, copolymers of quite uniform compositions were obtained also at higher conversions by gradual addition of the more reactive acryl ester during the progress of the copolymerization[6] and thus correcting the ratio of two monomers continuously. Indeed, the compositions of these copolymers are quite similar to those obtained at low conversions (Tables I and II).

Regarding the rates of copolymerization, determined gravimetrically, there is a steady decrease with increasing comonomer content for the three systems.

TABLE IV
Copolymerization Parameters for Esters of Acrylic Acid (M_1)
with Ethyl α-Cyanocinnamate (M_2)

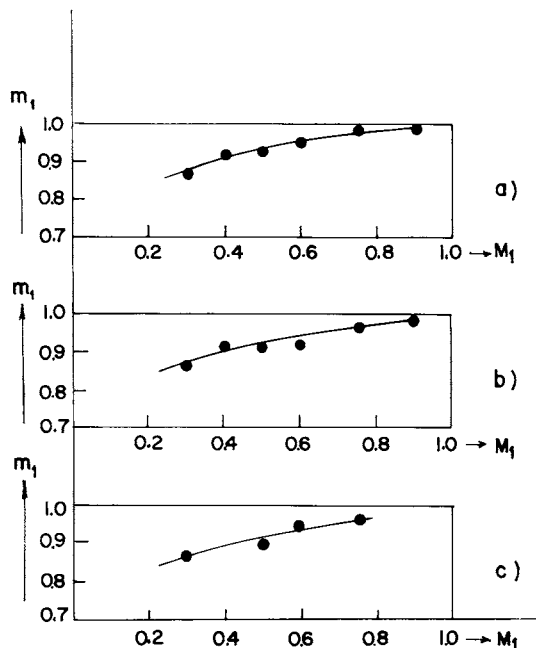|	Kelen–Tüdös method[8]	
Acrylic ester	Graphic	Least square
Methyl acrylate	$r_1 = 14.0$; $r_2 = 0.045$	$r_1 = 13.85$; $r_2 = 0.04$
Ethyl acrylate	$r_1 = 10.3$; $r_2 = -0.062$	$r_1 = 9.87$; $r_2 = -0.064$
Butyl acrylate	$r_1 = 8.4$; $r_2 = -0.074$	$r_1 = 8.6$; $r_2 = -0.066$

Fig. 4.   Copolymerization in toluene solution of ECC (M_2) with: (a) methyl acrylate (M_1); (b) ethyl acrylate (M_1); and (c) butyl acrylate (M_1). Initial copolymer composition versus composition of monomer feed.

Although of different polarity, the acrylate radicals seem to react preferably with another acrylate molecule because of steric factors of the rather bulky ECC monomer. Further, as already explained in a previous paper,[4] the ECC monomer, when attacked by a free radical, becomes a resonance stabilized radical, resulting in a decrease of its reactivity.
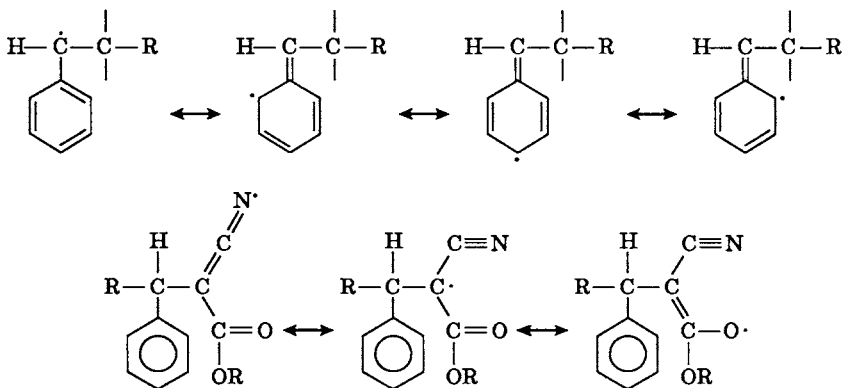
The acrylate radicals on the other hand are rather weakly stabilized:
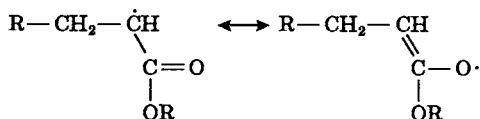
Due to the high rate of the homopolymerization of the acrylate esters,[1] the high acrylate content of the copolymers even at lower starting concentration can be explained. This behavior is quite similar to the copolymerization of ECC with acrylonitrile.[4]

The Alfrey–Price Q_2 and e_2 values[11] for ethyl α-cyanocinnamate with the three acrylate esters (Table V) were calculated according to equation:

$$r_1 = (Q_1/Q_2) \exp[-e_1(e_1 - e_2)] \qquad (2)$$

by using the r_1 values from the present paper and from the copolymerization of ECC with acrylonitrile.[4] The Q_2 and e_2 values obtained for ECC are somewhat lower for the copolymerization with the three acrylate esters in comparison to the values from the pair ECC–acrylonitrile.[4]

Characterization

IR Spectra

As a typical example of the now investigated systems, the spectrum of poly (methyl acrylate-co-ECC) containing 13 mol % of ECC (experiment no. 29) is shown in Figure 5.

The dominant carbonyl ester bands at 1740 and 1100–1250 cm^{-1} (C—O stretching) are due to the ester groups from both monomers, whereas the presence of the comonomer ECC is confirmed by the absorptions of the phenyl group at 1600 and 1490 cm^{-1} and the very weak absorption of the nitrile group at 2225 cm^{-1}. This "quenching" of the —C≡N absorption is known especially for compounds like ECC, having an oxygen-containing group attached to the same carbon atom as the nitrile.[14]

The 1430–1450 and 1370–1390 cm^{-1} absorptions belong obviously to the methylene and methyl groups, respectively.

TABLE V
Q and e Values of Ethyl α-Cyanocinnamate

Monomer	Q_2	e_2	Reference
Methyl acrylate	0.42	0.6	12
Ethyl acrylate	0.42	0.62	12
Butyl acrylate	0.43	0.52	12
Acrylonitrile	0.60	1.2	13
Ethyl α-cyanocinnamate	0.06	1.75	This paper[a]
	0.08	1.98	This paper[b]
	0.11	2.23	This paper[c]
	0.13	2.70	4
	0.14	2.44	4
	1.24	0.87	13

[a] From copolymerization with methyl acrylate.
[b] From copolymerization with ethyl acrylate.
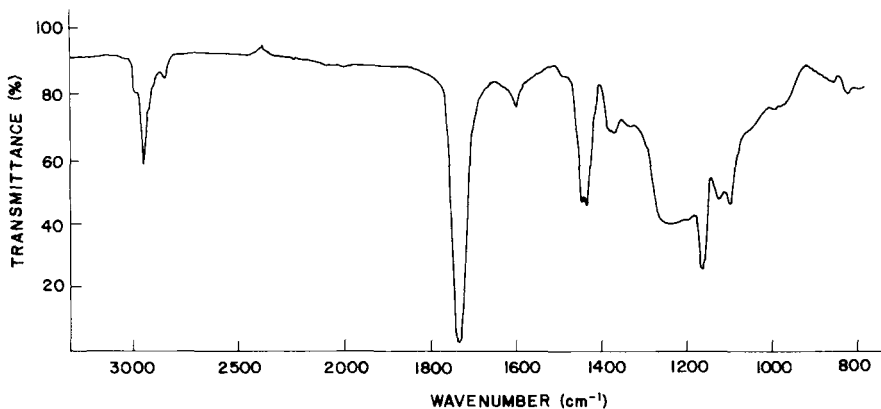[c] From copolymerization with butyl acrylate.

Fig. 5.   Infrared spectrum of copolymer methyl acrylate–ECC (experiment 29).

NMR of the Copolymers

Proton NMR spectra of the copolymers were obtained from their solution in CDCl$_3$ + TMS (Fig. 6). The singlet at 3.7 ppm belongs obviously to the —OCH$_3$ group, the absorptions between 1.8 and 2.3 ppm are assigned to the methylene and methine protons of the chain,[15] and the peak at 7.4 ppm is obviously due to protons of the aromatic ring. The relationship between the absorptions of the —OCH$_3$ group and the aromatic ring enables the determination of the composition of the copolymer.

Viscosity

For all three systems, there is a lowering of the intrinsic viscosity with increasing ECC content (Tables I–III). Similarly, such a decrease of the viscosity was also observed in the system acrylonitrile–ECC, even at rather low ECC concentration.[16]
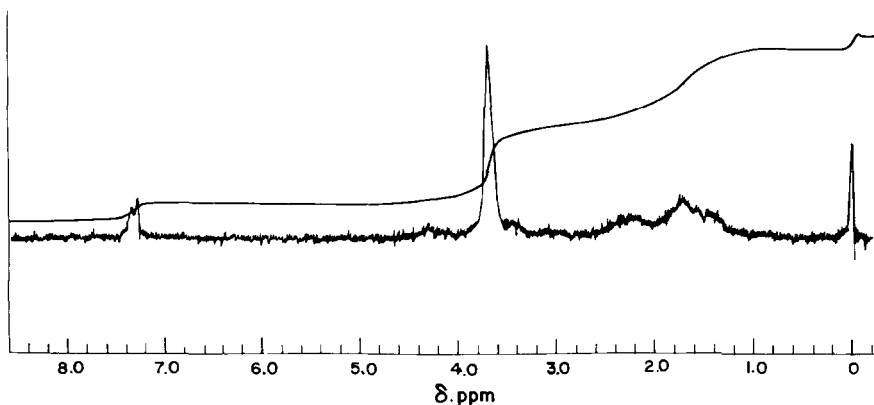

Fig. 6.   Proton NMR spectrum of copolymer methyl acrylate–ECC (experiment 29).

Glass Transition Temperature

The values of the glass transition temperature of the various copolymers of ECC with the three acrylate esters are actually of the same magnitude as the corresponding homopolyacrylates (Tables I–III), except for a small rise of T_g of poly(butyl acrylate-co-ECC), containing above 10 mol % ECC. Thus, whereas a small percentage of the polar and rather steric hindered ECC mer unit causes a considerable rise of the T_g in copolymers with styrene,[17] ECC seems to have little influence in the present acrylate ester systems. Yet, these rather low T_g values may be mainly due to the decrease of the molecular weight of the copolymers with rising ECC content, as indicated by the decrease of the intrinsic viscosity, causing an increase in the free volume and thus in the internal mobility.[18]

Solubility

All copolymers of the three investigated systems are soluble at room temperature in chloroform, methyl ethyl ketone, and toluene; they are insoluble in cyclohexane, hexane, and methanol, except the copolymer of butyl acrylate, which is slightly soluble in cyclohexane.

Regarding the possible use of these new copolymers as adhesives, the results of some preliminary tests will be reported in a subsequent paper.

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