

(2) It was established that the graph of the copolymerization constants as a function of σ_x will give 2 straight lines in all the examined cases of copolymerization, these intersecting at the point equivalent to the unsaturated styrene, and the slope of the line characterizes the polarity of the radical.

Translated by K. A. ALLEN

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COPOLYMERIZATION OF CROTONIC ACID WITH VINYLPIRROLIDONE*

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A DESCRIPTION is given in the literature of radical copolymerization of crotonic acid (CA) with acrylonitrile [1, 2], vinyl acetate [3-5], vinylidene chloride [4] and styrene [2]. Of the water-soluble copolymers, CA copolymers containing vinyl alcohol [6, 7] and vinyl-pyrrolidone (VP) are of the greatest interest. CA-VP copolymers were first synthesized by the authors [8] and used for reaction with certain physiologically active substances [9-12].

This paper describes the results of investigation of the radical copolymerization of CA with VP in the presence of azo-iso-butynodinitrile (AIB) and hydrogen peroxide.

* Vysokomol. soyed. **A9**: No. 8, 1807-1813, 1967.

Copolymer composition. CA-VP copolymers containing 5 to 47 mole% CA units were prepared. An azeotropic copolymer was formed with a CA content of 13 mole% in the initial mixture (Fig. 1). In the range of $M_2^0=80-100$ mole% VP the copolymer composition in practice conformed to the composition of the initial mixture; on increasing the CA content in the initial mixture a certain reduction was observed in the CA content in the copolymer, compared with its content in the initial mixture (Fig. 1).

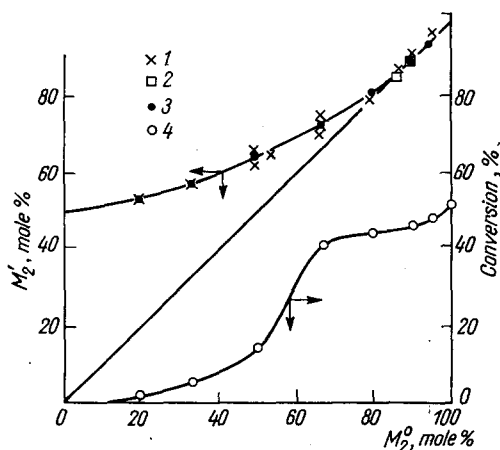


FIG. 1

FIG. 1. Dependence of the composition and yield of CA-VP copolymers on the composition of the initial mixture (80°): 1-3—curves of copolymerization: experimental points (1-0.5% AIB; 2-1% H_2O_2) and calculation curve for $r_1=0.02$ and $r_2=0.85$ (3); 4—copolymer yield in 50 min with 0.5% AIB.

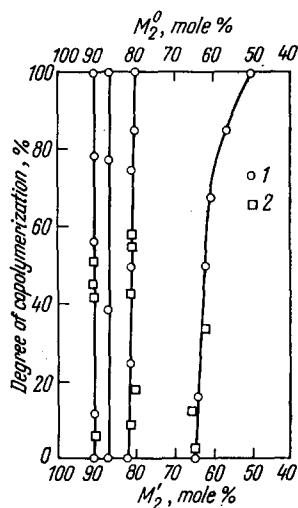


FIG. 2

FIG. 2. Diagram of the integral composition of copolymers; calculated (1) and experimental (2) points: M_2^0 —VP content in the initial mixture, M'_2 —VP content in the copolymer.

Copolymerization constants of the CA-VP system calculated by the method proposed by Finemann and Ross [13] and by selecting a curve [14], were as follows: $r_1=0.02 \pm 0.02$; $r_2=0.85 \pm 0.05$; $r_1 r_2=0.017$. Thus, both types of polymer radical, particularly the polymer radical ending with a CA unit, react considerably more quickly with another monomer than their own. It follows from a comparison of copolymerization data for crotonaldehyde (CAL)-VP ($r_2=0.5$) [15] and CA-VP ($r_2=0.85$) systems that, in the second case, the tendency of the polymer radical ending with VP to combine with its monomer (VP) is greater than in the CAL-VP system and therefore the CA-VP copolymer should have a less regular structure than the CAL-VP copolymer. From the copolymerization constants derived the relative activities, $1/r$, of monomers were calculated

in relation to radicals in the CA-VP system and a comparison made with the values derived for the CAI-VP system.

TABLE 1. RELATIVE ACTIVITIES OF MONOMERS
1/*r* IN RELATION TO VARIOUS RADICALS

Monomers	Radicals		
	VP	CA	CAI
VP	1	50	33.3
CA	1.175	1	—
CAI	2	—	1

TABLE 2. DEPENDENCE OF INTRINSIC VISCOSITY
OF CA-VP COPOLYMERS ON THE TEMPERATURE OF COPOLYMERIZATION
($M_2^0 = 80$ mole% VP; 3.5 hr)

Amount of AIB, %	[η] of copolymers obtained	
	at 65°	at 80°
0.05	0.38*	0.32*
0.2	0.32	0.255
0.5	0.24	0.17
2.0	—	0.10

* Measured in 0.02 N HCl.

Table 1 indicates that the relative activity in relation to the VP radical, in relation to the vinylidene chloride radical [4, 16], is lower for the CA monomer than for the CAI monomer.

Diagrams showing CA-VP copolymer composition (Figs. 2 and 3) characterize all the possible cases of behaviour of components in this pair. The integral composition (average composition of copolymers obtained with a given degree of conversion), calculated from an approximate integral equation of composition (Medvedev and Abkin) [17, 18] in a corrected form [19], satisfactorily agrees with experimental data (Fig. 2). Both the differential composition (composition of copolymers formed at a given moment) and the integral composition, in a range close to the azeotropic, hardly vary with the degree of conversion, being basically determined by the composition of the initial mixture.

Rate of copolymerization. The main factor determining the rate of copolymerization of this pair is the composition of the initial mixture. The overall rate of copolymerization (copolymer yield in 50 min) (Fig. 1, curve 4) slightly de-

TABLE 3. DEPENDENCE OF INTRINSIC VISCOSITY OF CA-VP COPOLYMERS ON THE AMOUNT OF INITIATOR (50 min 80°)

Amount of AIB, %	[η] at M_2^0 of:				
	100	95.2	90.9	80	66.7
0.5	0.45	0.23 *	0.19	0.17	0.11
0.1	0.52	0.41 *	0.38	0.2 *	0.18
0.05	—	—	0.35 *	0.24 *	—
0.02	—	0.46 *	—	—	—

* Measured in 0.02 N HCl.

creases with an increase in CA content in the initial mixture in the range of 5–20 mole% CAI (where the copolymer composition is close to the azeotropic) and markedly decreases on further increasing CA content.

Intrinsic viscosity. A study was made of the effect of composition of the initial mixture, amount of initiator, degree and temperature of copolymerization on the intrinsic viscosity of CA-VP copolymers (measured in water and 0.02 N HCl). A reduction in the temperature of copolymerization (Table 2) and the amount of initiator (Tables 2 and 3) increases intrinsic viscosity, which is typical of radical polymerization. An increase in duration, i.e. degree of copolymeriza-

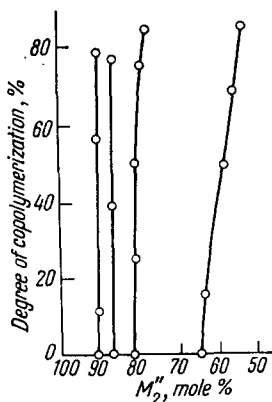


FIG. 3

FIG. 3. Diagram of differential composition of copolymers: M_2'' —VP content in the copolymer.

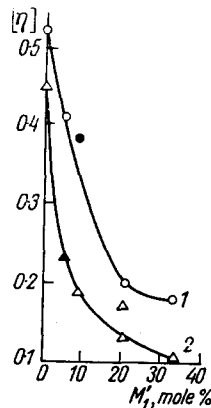


FIG. 4

FIG. 4. Dependence of the intrinsic viscosity of CA-VP copolymers (in water and 0.02 N HCl) on the composition of the initial mixture (80°, 50 min): 1—0.1% AIB; 2—0.5% AIB; dark points—in 0.02 N HCl.

tion does not alter the intrinsic viscosity of copolymers. The intrinsic viscosities of CA-VP copolymers depend a great deal on the composition of the initial mix-

ture. An increase in CA content in the initial mixture and consequently in the CA-VP copolymer (Fig. 4), as also for CA-vinyl acetate copolymers [3], produces a reduction in intrinsic viscosity.

The concentration dependence of the reduced viscosity (η_{sp}/c) of CA-VP copolymers of different composition and molecular weight obtained both in the presence of AIB and hydrogen peroxide was investigated. For aqueous solutions of CA-VP copolymers, which have relatively higher molecular weights ($[\eta] > 0.3-0.4$) and low CA contents, an increase was observed in the value of η_{sp}/c with dilution, i.e. a polyelectrolyte effect was observed. In the case of aqueous (and alcoholic) solutions of low molecular weight CA-VP copolymers ($[\eta] = 0.08-0.25$) and copolymers over 5-10 mole% CA, a linear decrease was observed in the reduced viscosity values with dilution, which is typical of conventional polymers (Fig. 5).

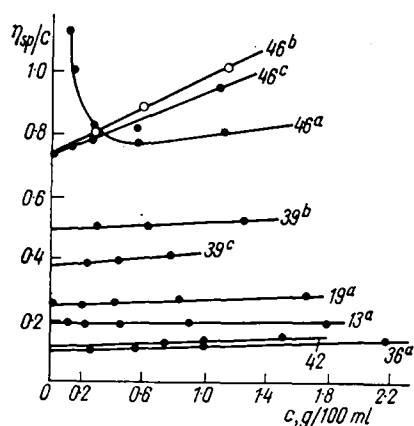


Fig. 5. Dependence on reduced viscosity (η_{sp}/c) of CA-VP copolymers on concentration; measured in water (a), 0.02 N HCl (c) and methanol (b)

No.	M_2^0	AIB, %	Temperature, °C	Time, hr	M_2' , mole%
46	90.9	0.05	65	3.5	90
39	80	0.05	65	3.5	79.5
19	80	0.2	80	3.5	81.3
13	80	0.516	80	0.83	81.2
36	80	2.0	80	0.83	82.3
42	86.5	H ₂ O ₂ —1%	80	3.5	86.5

Similar results were obtained by Lyubina and Strelina* for copolymers with $[\eta]$ of 0.2 (Fig. 6), whereby it was established that intrinsic viscosities remained

* We express our gratitude to S. Ya. Lyubina and I. A. Strelina for the information kindly provided.

the same even on changing the ionic strength of the solution (water, 0.02 N NaCl, 0.2 N NaCl, 1 N NaCl).

When investigating the concentration dependence of η_{sp}/c of CA-VP copolymers neutralized by addition of NaOH ($\alpha=1$) in aqueous solution an increase was observed in the values of η_{sp}/c with dilution, whereas in solutions in 1 N and 0.1 N NaCl a linear drop in reduced viscosity with dilution was revealed; the absolute values of η_{sp}/c in water in the whole concentration range exceed these values for solutions with ionic strengths of 0.1 N and 1 N NaCl. With the same ionic strength (1 N NaCl) (see curve 4 in Fig. 6) the intrinsic viscosity of this copolymer in neutralized form ($\alpha=1$) is higher than in the un-ionized state ($\alpha=0$) (curve 1). Experimental data do not enable a sufficiently reliable explanation of this anomaly to be given—the absence of a polyelectrolyte effect in low-molecular weight CA-VP copolymers. This problem requires further study. It is not impossible, however, that associates are formed in CA-VP copolymers between CA and VP units by the hydrogen bond formed between the carbonyl of the amide group of VP and the OH group of the CA carboxyl, and it is this interaction which hinders the ionization of carboxyl groups in copolymers and prevents the polyelectrolyte effect. The formation of a hydrogen bond between the carbonyl oxygen of poly-

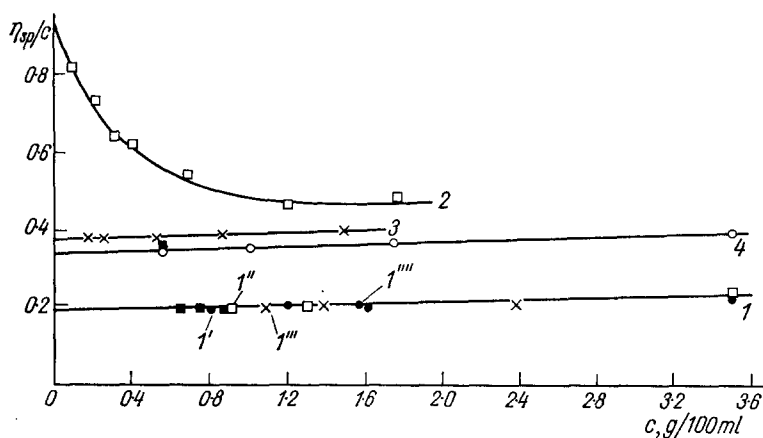


FIG. 6. Dependence of reduced viscosity (η_{sp}/c) of CA-VP copolymer No. 28 ($M_1^0=20$ mole%; $M_1=18.6$ mole%; AIB—0.5%, 65°C) on concentration in solvents with varying ionic strength: 1— $\alpha=0$, 1'— H_2O , 1''—1 N NaCl, 1'''—0.2 N NaCl, 1''''—0.02 N NaCl; 2— $\alpha=1$, $H_2O+NaOH$ (1 : 1); 3— $\alpha=1$, 0.1 N NaCl+NaOH (1 : 1); 4— $\alpha=1$, 1.1 N NaCl+NaOH (1 : 1).

vinyl pyrrolidone (PVP) and the hydroxyl group of acids was observed during the decantation of solutions of PVP and organic acids [20]. It is also possible that the hydrogen bonds in the copolymer are stabilized by the hydrophobic interaction between the methyl groups, as observed in polymethacrylic acid [21].

TABLE 4. DISTRIBUTION OF CROTONIC ACID, CROTONALDEHYDE AND VINYL PYRROLIDONE UNITS IN MACROMOLECULES OF CA-VP AND CAI-VP COPOLYMERS

Type of copolymer	Copolymerization constants		M_1^0 , mole %	Content of various types of bonds in the copolymer (f), mole %				Number of monomer units	
	r_1	r_2		M_1-M_1	M_1-M_2	M_2-M_1	M_2-M_2	\bar{L}_1	$\bar{L}_2(VP)$
CA-VP	0.02	0.85	13.27 Azeotrope	0.04	13.23	13.23	73.5	1.003	6.55
CAI-VP	0.02	0.85	20	0.1	18.5	18.5	62.9	1.005	4.4
	0.03	0.5	10	0.05	15.38	15.38	69.19	1.003	5.51
	0.03	0.5	34 Azeotrope	0.5	33.5	33.5	32.5	1.015	1.97

TABLE 5. STRUCTURE OF A CA-VP AZEOTROPIC COPOLYMER

n	Structure M_1	F_1 , mole %	n	Structure M_2	F_2 , mole %	n	Structure M_2	F_2 , mole %
1	$\sim M_1 \sim$	13.13	1	$\sim M_2 \sim$	2.02	10	$\sim (M_2)_{10} \sim$	4.54
2	$\sim M_1 M_1 \sim$	0.08	2	$\sim (M_2)_2 \sim$	3.44	11	$\sim (M_2)_{11} \sim$	4.24
3	Others	0	3	$\sim (M_2)_3 \sim$	4.35	For units with $n=1-11$		49.16
			4	$\sim (M_2)_4 \sim$	4.91	Others		37.57
			5	$\sim (M_2)_5 \sim$	5.21	20	$\sim (M_2)_{20} \sim$	1.72
			6	$\sim (M_2)_6 \sim$	5.31	21	$\sim (M_2)_{21} \sim$	1.545
			7	$\sim (M_2)_7 \sim$	5.22	30	$\sim (M_2)_{30} \sim$	0.485
			8	$\sim (M_2)_8 \sim$	5.08	40	$\sim (M_2)_{40} \sim$	0.126
	Total	13.27	9	$\sim (M_2)_9 \sim$	4.84	Total		86.73

Structure of copolymers. Distribution of monomer units in the macromolecule. The copolymerization constants being known, the structures of azeotropic and initial copolymers can be calculated. The composition of a CA-VP azeotropic copolymer, calculated by the Wall formula [22] is: $M_1^0=13.27$ mole %; $M_2^0=86.73$ mole %. The intramolecular distribution of units of both monomers in the macro-

molecule (probability of all possible types of monomer bonds) for an azeotropic copolymer and for an initial copolymer (in the case when in the composition of the initial mixture $M_1^0=20$ mole % and $M_2^0=80$ mole %), calculated from the formulae derived by Wall [22] and Medvedev [17, 18], is shown in Table 4.

Table 4 indicates that in both copolymers the CA and CAI basically contain one monomer unit each. Using the formulae proposed by Medvedev [16, 17] for the calculation of distribution functions, F_1 and F_2 (i.e. by determining the molar content in the macromolecular chain of CA and VP units formed of n identical monomer units), we obtain the azeotropic CA-VP copolymer structure shown in Table 5. Thus, as regards VP units, the CA-VP azeotropic copolymer has a more irregular structure than the croton-aldehyde-VP copolymer [15]. In the azeotropic CA-VP copolymer of 86.7 mole % VP, 49 are grouped with 1-11 monomer units; we have on an average $L_2=6.55$ VP monomers in the unit. For the azeotropic CA-VP copolymer we have an average of 1.97 monomer units per VP unit.

Characteristics of CA-VP copolymers. CA-VP copolymers are white powders, or fibrous (according to molecular weight) substances. They are soluble in water, alcohols (methyl, ethyl, butyl), in acetic acid, swell in chloroform, are insoluble in acetone, ethyl acetate, diethyl and petroleum ethers, benzene, toluene, carbon tetrachloride, hexane, dioxane, etc. With the increase of content of CA units in copolymers, their solubility in water decreases; copolymers containing 35 mole % CA and more are insoluble in water. Transparent, colourless films can be obtained from the copolymer solutions.

EXPERIMENTAL

VP—produced by Lawson (Great Britain), b.p. $70^\circ/5$ mm, d_{20}^{20} 1.048; bromine number 143-146; n_D^{20} 1.5117-1.5130. CA—m.p. $72-72.5^\circ$, acid number 651.5; bromine number 187.

AIB—obtained after repeated recrystallization; melting point 105° . Hydrogen peroxide 30% aqueous solution. Concentration was determined with permanganate [23].

Copolymerization was carried out in bulk, in ampoules at 65 and 80° in the presence of 0.01-1% AIB and 1-1% hydrogen peroxide as initiators. The copolymers obtained were precipitated with ether from ethanol solution, reprecipitated twice, extracted with ether and dried *in vacuo* to constant weight. Copolymer composition was established from analytical data by determining the acid and bromine numbers. In certain specimens the nitrogen content was determined using the Dumas micro-method and IR spectra (absorption in the 1720 cm^{-1} region is typical of the CO-group of CA). Acid number was determined by titration of an aqueous or, better, an alcoholic copolymer solution with a 0.1 N NaOH, or KOH solution, respectively, in the presence of phenolphthalein or potentiometrically. The results obtained were identical. The viscosity of CA-VP solutions was determined (in water, methanol, ethanol, 0.02 N HCl) at 20° . Intrinsic viscosity in water for most CA-VP copolymers is somewhat lower than the values observed in methanol and ethanol (Fig. 5).

The purification of copolymers from unreacted monomers was confirmed both by bromination (bromine numbers were zero in practice), and by IR spectra (absence of absorption at 1640 cm^{-1} , typical of the double bond). Similar results regarding IR spectra, bromine numbers and neutrality (acid number was zero; absence of absorption at 1720 cm^{-1}) were obtained for control specimens made of a PVP + CA mixture (4 : 1) heated and purified under conditions used for copolymers.

CONCLUSIONS

(1) A study was made of the radical copolymerization of crotonic acid with vinylpyrrolidone. Water-soluble copolymers of crotonic acid and vinylpyrrolidone were obtained which contain 5–35 mole % crotonic acid. It was established that the composition, yield and intrinsic viscosity of copolymers depend on polymerization conditions.

(2) Copolymerization constants of the crotonic acid–vinylpyrrolidone system were calculated ($r_1=0.02\pm0.02$; $r_2=0.85\pm0.05$; $r_1\cdot r_2=0.017$).

(3) The intramolecular distribution of monomers in the macromolecule was calculated for azeotropic and initial copolymers. It was found that in both cases the crotonic acid units basically contain 1 monomer unit each. It was found that azeotropic copolymers of crotonic acid with vinylpyrrolidone are more irregular in structure in respect of vinylpyrrolidone units than azeotropic copolymers of crotonaldehyde with vinylpyrrolidone.

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THE CORRESPONDING STATES THEORY OF POLYMER SOLUTIONS AND THE THERMODYNAMICS OF POLYMERIC-GLASS-SOLVENT SYSTEMS

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THE feeling seems to exist among polymer chemists that accepted polymer solution theory deals adequately with all essential features of polymer solution behaviour, and that future progress will be confined to details. However, phenomena have been discovered recently which are at variance with the predictions of the usual theory, as for instance: (a) the change of the Flory-Huggins polymer-solvent interaction parameter χ_1 with concentration [1] (Fig. 1); (b) a negative, exothermic heat of mixing a liquid polymer and a solvent has been observed, not only in polar systems, but also for non-polar polymers with non-polar solvents [2-3]; negative entropies and heats of dilution are also found [3]. Very large negative heats and entropies of dilution are observed in systems involving a glassy polymer [4] as will be discussed later. (c) Even non-polar polymer-solvent systems separate into two phases when the temperature is increased sufficiently as well as when it is lowered [3, 5]. Thus solvent "quality" does not increase monotonically with temperature as expected from the quasi-lattice theories, but passes through a maximum and then decreases.

The typical phase diagram in Fig. 2 shows this recently discovered phase separation occurring at temperatures above a lower critical solution temperature (LCST), and the well-known separation below the upper critical solution temperature (UCST). For a polymer of infinite molecular weight, the latter temperature is the Flory θ -point. Both coexistence curves in Fig 2 are strongly asymmetrical, that is, the critical concentration ϕ_2 is small. With increase of the molecular

* *Vysokomol. soyed.* A9: No. 8, 1814-1825, 1967.