SOME ASPECTS OF THE COPOLYMERIZATION OF VINYLACETATE AND BUTYLACRYLATE*

A. F. Nikolayev, L. P. Vishnevetskaya, O. A. Gromova, M. M. Grigor'eva
and M. S. Kleshcheva

Scientific Research Institute for Polymerized Plastics

THE system vinylacetate–butylacrylate (VA–BA) is the least studied theoretically of all the pairs of monomers containing vinylacetate and esters of acrylic acid, although it is used technically. The copolymerization constants r_1 and r_2 have not been determined for this pair of monomers because of experimental difficulties. As a monomer with an unconjugated double bond, VA has for a long time attracted the attention of investigators. Values for the specific activity $Q=0.026$ and for the polarity of its radical $e=-0.22$ have been established for VA [1]. The fact that there is no conjugation of the unpaired electron of the VA radical with the carbonyl group makes the radical extremely reactive and is accompanied by a high rate for the radical's deactivation. The "life time" of the VA radical is less than 0.02 sec whereas that of the butylacrylate radical is up to 0.2 sec [2]. The high reactivity of the radical leads to the high sensitivity of VA towards the presence of micro-impurities (active chain-transfer agents) which cannot be determined analytically in a number of cases. The polymerization and co-polymerization of VA is practically always preceded by an induction period, and it is very difficult to obtain reproducibility in kinetic relationship [3].

In copolymerization with vinyl compounds having a double bond more readily polarized than that of VA, the VA radical adds on more actively to the other vinyl compound than to its own less active monomer. As a result of this, the reactivity ratio for VA is very small for such pairs of monomers [4]. A characteristic feature of the copolymerization of VA with these monomers is the existence of extrema on the curve showing how the rate of the process depends on the composition of the monomer mixture [5], the extreme values being determined by the concentration ratios of the two monomers and of the two types of radical.

VA forms copolymers with arcylic acid and with its esters, but in all cases the acrylates are more reactive components in copolymerization than VA (Table 1).

TABLE 1. COPOLYMERIZATION CONSTANTS r_1 AND r_2 AND THE RELATIVE RATE
OF ADDITION $(1/r_1)$ OF ACRYLIC ACID AND ITS ESTERS TO THE VA RADICAL

Monomer M_2	r_1	r_2	$1/r_1$	Reference
Acrylic acid	0.01 ± 0.03	10 ± 1	100	[6]
	0·1	2	10	[7]
Methylacrylate	0.1 ± 0.1	9 ± 2.5	10	[8]
	0.5 ± 0.06	3 ± 0.3	2	[9]
2-Ethylhexylacrylate	0.14 ± 0.1	6.24 ± 0.1	7·1	[10]

Let us note the fact that there is a considerable discrepancy between the values of the monomer reactivity ratios obtained by different investigators. As the length of the aliphatic group in the acrylic ester molecule is increased, the relative rate of its copolymerization with VA falls markedly [11].

Monomer	methylmethacrylate	ethylacrylate	butylacrylate
Relative rate of copolymerization	1·1	0·7	0·6

The low reactivity of acrylates in copolymerization with VA may be explained by the decreased conjugation of the double bond with the carbonyl group, because of the increased inductive effect of the alkyl group [12]. In fact, a tendency towards a reduction in the factor Q is observed in the series of derivatives of acrylic acid (Table 2) [1]. However, BA should have lower values of the parameters Q and e than those which are shown in Table 2.

TABLE 2. SPECIFIC ACTIVITY (Q) AND POLARITY (e)
OF ACRYLIC ACID AND ITS ESTERS [1]

Monomers	Q	e
Acrylic acid	1·15	0·77
Methylacrylate	0·42	0·60
Ethylacrylate	0·52	0·22
Butylacrylate	0·51	1·02
2-Ethylhexylacrylate	0·18	0·46

Chromatographic analysis of the monomer mixtures, supplemented by gravimetric determination of the copolymer yield, was used in the present work to determine the change in the VA and BA monomer contents accompanying their copolymerization. Table 3 presents results which make it possible to calculate the copolymerization constants from the Fineman–Ross equation [13] by the method of least squares: these were found to be $r_1=0.06\pm0.01$ and $r_2=3.07\pm0.3$. The specific reactivity of BA $Q=0.33$ and the polarity of its radical $e=1.08$ were determined from the Alfrey–Price equation [14]. The value obtained

for the factor Q fits in well with the series of values for the derivatives of acrylic acid (Table 2) and gives evidence of the low degree of conjugation of the double bond with the carbonyl group, the conjugation being weakened by the considerable inductive effect of the butoxyl radical. The high values obtained for the polarity of the BA radical are in good agreement with data presented previously.

The values found for r_1 and r_2 indicate that VA is the less reactive component in the monomer pair being investigated, and that its addition to the "foreign" radical proceeds much more rapidly than to its own radical $(1/r_1 = 17)$.
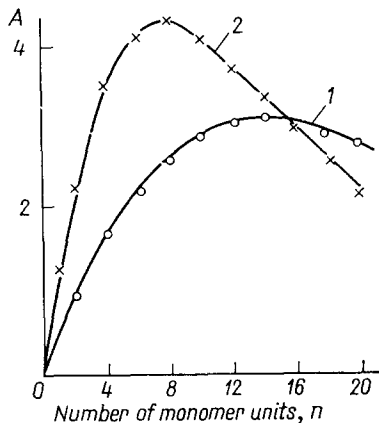

Fig. 1

Fig. 2

Fig. 1. Proportion of structures of the type $n \cdot BA$ in VA–BA copolymers: 1 — BA : VA $= 80 : 20$, 2 — BA : VA $= 70 : 30$; A is the mole fraction of the corresponding structure.
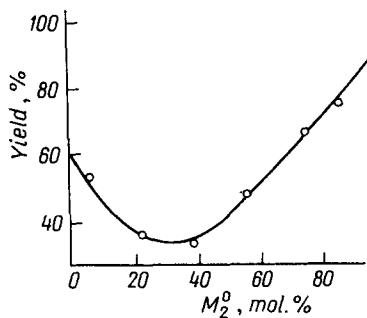
Fig. 2. Dependence of the yield of the VA–BA copolymer on the composition of the original mixture. $M^0{}_2$ is the concentration of BA in the original mixture.

Table 4 gives results of calculation by Medvedev's method [15] of the probability of forming various structures in the VA–BA copolymer (f) and the average length made up of each monomer unit (L) as a function of the composition of the initial mixture; these data indicate that even with a considerable excess of VA in the initial mixture, the copolymer macromolecules contain only individual VA units. The marked difference between the reactivity of the VA and BA monomers leads to the copolymer composition's being highly sensitive to the composition of the initial mixture.

For example, when the VA : BA ratio is decreased by 10 mole% (from 50 : 50 to 40 : 60), the probability of forming BA–BA links rises by a factor of 5. A feature of copolymers formed with an excess of BA in the reaction mixture is their polydispersity with respect to the size of sequences, since practically all structures of the type $n \cdot BA$ from $n = 1$ to $n = 20$ are present in the macromolecule in equal proportions (Fig. 1).

TABLE 3. DATA CONCERNING THE COPOLYMERIZATION OF VINYLACETATE (M_1) AND BUTYLACRYLATE (M_2)

Quantity of monomer taken				Molar ratio M_1^0/M_2^0	Conversion, %	Monomer contents in copolymer				Unreacted monomers			
g		mmole				g		mmole		g		mmole	
M_1^0	M_2^0	M_1^0	M_2^0			M_1'	M_2'	M_1'	M_2'	M_1	M_2	M_1	M_2
3·5299	5·3660	41·0024	41·8663	1·0	12·3	0·1611	0·9331	1·8712	7·2801	3·3688	4·4329	39·1311	34·586
7·7903	1·3694	90·4901	10·6842	8·0	5·5	0·1629	0·3441	1·8922	2·6847	7·6274	1·0253	88·5979	7·9995
8·2648	1·1536	96·0018	9·1000	10·5	7·4	0·2403	0·4566	2·7920	3·5624	8·0860	0·6970	93·4100	5·4380
8·1388	1·1036	94·5382	8·6104	11·0	12·7	0·7130	0·4640	8·2820	3·6201	7·4258	0·6396	86·2563	4·9902
9·0294	0·5306	104·8832	4·1398	25·0	8·2	0·4796	0·3024	5·5709	2·3593	8·5498	0·2282	99·3123	1·7804

TABLE 4. PROBABILITY OF FORMATION OF VARIOUS STRUCTURES (f), AVERAGE LENGTH (L) AND INTRAMOLECULAR DISTRIBUTION IN COPOLYMERS OF VA (M_1) WITH BA (M_2)

$M_1^0:M_2^0$ (molar)	$f_{M_1-M_1} \times 10^2$	$f_{M_1-M_2} = f_{M_2-M_1} \times 10^2$	$f_{M_2-M_2} \times 10^2$	L_{M_1}	L_{M_2}	Mole fraction of M_1 structures with various $n \times 10^2$						Mole fraction of M_2 structures with various $n \times 10^2$					
						1	2	3	4	5	Σ	1	2	3	4	5	Σ
10:90	0·022	3·374	93·229	1·00	29·60	—	—	—	—	—	—	—	—	—	—	—	—
20:80	0·105	6·995	85·904	1·01	13·27	6·88	0·20	0·00	0·00	0·00	7·08	0·65	0·99	1·39	1·73	2·02	6·78
30:70	0·280	10·882	77·955	1·25	8·16	10·60	0·53	0·02	0·00	0·00	11·15	1·33	2·30	3·08	3·60	3·90	14·21
40:60	0·602	15·049	69·315	1·04	5·60	—	—	—	—	—	—	—	—	—	—	—	—
50:50	1·169	19·493	59·844	1·06	4·07	18·39	2·09	0·18	0·01	0·00	20·67	47·89	7·37	8·74	8·22	8·39	80·10
60:40	2·175	24·174	49·476	1·09	3·04	22·17	3·66	0·45	0·05	0·01	26·33	7·93	10·66	10·74	9·63	8·08	54·64
70:30	4·051	29·000	38·404	1·14	2·32	25·43	6·23	1·15	0·19	0·03	33·03	12·47	14·21	12·15	9·22	6·57	47·07
80:20	8·000	33·250	25·511	1·24	1·76	—	—	—	—	—	—	—	—	—	—	—	—
90:10	18·740	34·708	11·839	1·54	1·34	34·36	24·06	12·67	5·95	2·59	79·63	13·85	13·17	5·02	1·70	0·54	34·70

For the copolymerization of VA with BA, a minimum is found on the curve showing how the rate of the process depends on the composition of the initial mixture (Fig. 2). This phenomenon is explained by the fact that, if the concentration of either of the monomers in the copolymerizing mixture is large, a high reaction rate is caused by the facility of a particular interaction: in the case
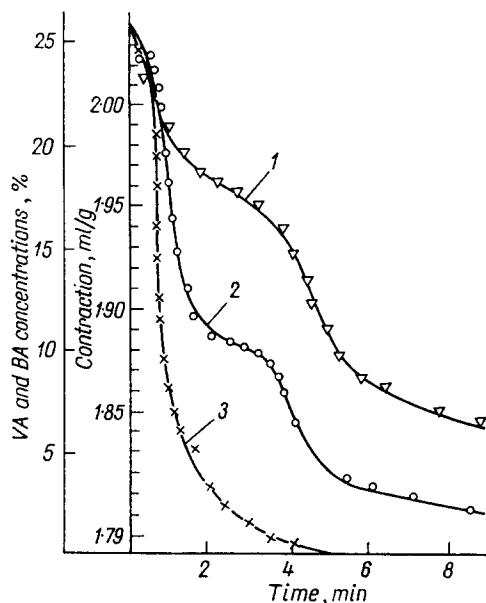

Fig. 3. Dependence of the concentration of the monomers and the contraction on the duration of polymerization: 1—concentration of VA, wt.%; 2—concentration of BA, wt.%; 3—contraction, ml/g.

of a high concentration of VA, this interaction is between a reactive radical and its own unreactive monomer, and in the case of BA, between an unreactive radical but with its own reactive monomer. At low concentrations of BA, when the interaction between its radical of low reactivity and a monomer of the same chemical nature is improbable, the overall copolymerization rate is determined by the low rate of interaction between this unreactive radical and the VA monomer of low reactivity. There thus exists a certain ratio of the initial monomers such that the rate of copolymerization should be a minimum. In the case investigated, this ratio is VA : BA=30 : 70. However, during copolymerization the composition of the monomer mixture is continuously changing because of the more rapid consumption of the more reactive monomer, and consequently for certain concentration ratios conditions may be realized which correspond to the composition of the monomer mixture giving the minimum copolymerization rate. This should lead to a retardation of the copolymerization process which will prevail when a sufficient quantity of the more reactive macroradicals has accumulated in the mixture. This phenomenon should be observed in all

cases when the way in which the copolymerization rate depends on the composition of the monomer mixture exhibits an extreme value, and is accompanied by the formation of copolymers with a reduced molecular weight when retardation occurs.
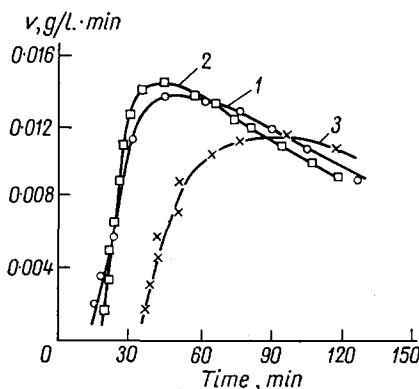

FIG. 4. Change in the rate (v) of copolymerization for the copolymerization of VA and BA in the following solvents: *1*—ethyl acetate, *2*—toluene, *3*—ethyl alcohol.

We observed this effect during the copolymerization of a mixture consisting of 60 mole % VA and 40 mole % BA in ethylacetate (EA) in the presence of 0·2% ABIN at 70°C (molar ratio EA : monomer mixture=1 : 1). This retarding effect is clearly seen from the formation of a plateau on the kinetic curves. Figure 3 shows curves giving the separate changes in the VA and BA concentrations during copolymerization, together with the dilatometric curve for the change in the volume of the copolymerizing mixture.

A kinetic feature of the copolymerization of VA and BA is the absence of a period of constant rate even when the reaction is carried out in solvents (Fig. 4).

For the pair of monomers studied, ethyl alcohol is the most active chain-transfer agent without causing termination of the kinetic chain, and ethylacetate is the least active. Concentrated solutions of the copolymer with a fairly high molecular weight have a low viscosity in toluene (Table 5).

TABLE 5. INTRINSIC VISCOSITY [η] AND YIELD OF VINYLACETATE–BUTYLACRYLATE COPOLYMERS (MOLAR RATIO 60 : 40) OBTAINED IN VARIOUS SOLVENTS (70°C; initiator, 0·2% ABIN; ratio of solvent to sum of the monomers, 1 : 1)

Solvent	Yield after 9 hr	[η], dl/g	Viscosity of 40% solution, centipoise
Ethylacetate	96	0·9	22,000
Ethyl alcohol	94	0·3	200
Toluene	78	0·6	200

EXPERIMENTAL

The monomers and solvents were distilled twice before being used. The monomer and solvent fractions used in this work had constants corresponding to the data given in the literature.

In order to determine the monomer reactivity ratios, copolymerization was carried out in bulk in glass ampoules with a capacity of 20 ml at 70°C in the presence of 0·05 % azobisisobutyronitrile (ABIN). The monomer mixtures were prepared initially in the flask, and the calculated quantity of ABIN was introduced into the mixture. After the components had been carefully mixed, a sample was taken from the flask in which the concentration of each monomer, C_1^0 and C_2^0, was determined chromatographically. (A Griffin and George chromatograph was used in the present work; stationary phase, tricresylphosphate (20%) on diatomaceous brick; carrier-gas, helium). 10 ml of the mixture from the flask was introduced by means of a syringe into carefully prepared weighing ampoules, and the weight G of the monomer mixture (in grammes) was determined by weighing. After the ampoule had been purged five times with helium and evacuated, it was sealed and the copolymerization carried out. At the end of the process and after careful mixing, the ampoules were unsealed and 2 ml of the reaction mixture were taken out of the ampoule by means of a syringe; this was then dissolved in 10 ml of benzene. After dissolution, the concentration of each monomer (C_1, C_2) was determined in the mixture chromatographically.

At the same time as this, a sample (3–5 g) was taken from each ampoule and the copolymer yield P (in grammes) was determined from this. The molar fraction of each of the components going to make up the polymer was determined from the following equation:

$$m = \frac{P \cdot C + G(C^0 - C)}{M}$$

where M is the molecular weight of the monomer.

A comparison of the determination of the composition of a monomer mixture chromatographically and by gravimetric methods showed that the error in determining the concentration chromatographically did not exceed 3%.

CONCLUSIONS

(1) The monomer reactivity ratios for the copolymerization of vinyl acetate (VA) and butylacrylate (BA) have been determined: $r_{VA} = 0·06 \pm 0·01$ and $r_{BA} = 3·07 \pm 0·3$. The specific activity $Q = 0·33$ and the polarity $e = 1·08$ were calculated for BA.

(2) Some special features of the copolymerization of VA and BA in bulk and in solutions have been clarified: these consist in the high polydispersity of the copolymers with respect to composition and average length of sequences of monomer units. An effect involving the kinetic retardation of the reaction during the copolymerization of these monomers has been established.

Translated by G. F. MODLEN

REFERENCES

1. **L. J. JONNG**, J. Polymer Sci. 54: 439, 1961
2. **T. TSURUTA**, Reaktsii polucheniya sinteticheskikh polimerov (Reactions for the Synthesis of Synthetic Polymers). Goskhimizdat, 1963
3. **K. TYUDESH**, Vysokomol. soyed. A9: 2287, 1967

4. S. N. USHAKOV, Polivinilovyi spirt i yego proizvodnyye (Polyvinyl Alcohol and its Derivatives). Izd. AN SSSR, 1960
5. A. F. NIKOLAYEV, S. N. USHAKOV and L. P. VISHNEVETSKAYA, Vysokomol. soyed. 4: 1054, 1962 (Not translated in Polymer Sci. U.S.S.R.); J. R. TICHY, J. Polymer Sci. 33: 553, 1958; A. N. AKOPYAN and T. Ye. KREBKYAN, Vysokomol. soyed. 5: 201, 1963 (Translated in Polymer Sci. U.S.S.R. 4: 4, 818, 1963)
6. J. BOURDAIS, Bull Soc. Chim. France, No. 4, 485, 1955
7. T. ALFREY, J. J. BOHRER and H. MARK, Sopolimerizatsiya (Copolymerization). Foreign Languages Publishing House, 1956 (Russian translation)
8. F. R. MAYO, J. Amer. Chem. Soc. 70: 1519, 1948
9. I. S. AVETISYAN, V. I. YELISEYEVA and O. G. LARIONOV, Vysokomol. soyed. A9: 570, 1967 (Translated in Polymer Sci. U.S.S.R. 9: 3, 640, 1967)
10. J. MINTZER, Plast und Kautschuk 10: 250, 1963
11. Encyclopedia of Polymer Science, v. 1, p. 272, 1964
12. J. MATHIEU and A. ALLAIS, Printsipy organicheskogo sinteza (Principles of Organic Synthesis). Foreign Languages Publishing House, 1962 (Russian translation)
13. M. FINEMAN and D. ROSS, J. Polymer Sci. 5: 269, 1950
14. T. ALFREY and J. PRICE, J. Polymer Sci. 2: 101, 1947
15. L. M. GINDIN, A. D. ABKIN and S. S. MEDVEDEV, Dokl. AN SSSR 56: 177, 1947

ELECTROPHILIC AND NUCLEOPHILIC REACTIONS OF HALOGENOMETHYLATED STYRENE–DIVINYLBENZENE COPOLYMERS WITH 1-PHENYL-3-METHYLPYRAZOLONE-5 AND ITS DERIVATIVES*

G. V. Kharitonov and L. P. Belikova

Voronezh Technological Institute

(*Received* 30 *September* 1968)

For the removal of separate cations and anions, organic reagents have been recently used which have complex-formation properties. 1-phenyl-3-methylpyrazolone-5 (PhMP) and 1-phenyl-2,3-dimethylpyrazolone-5 (PhDMP) belong to this group of compounds. The type of complex formed in the system, M–R–X, depends on the pH of the medium, on the strength of the M–X and R–H bonds and on the geometrical dimensions of the cation and anion [1]. PhMP and PhDMP are susceptible to electrophilic substitution reactions in the 4-position [2, 3].

In a number of cases, the reactivity of the chlorine atom in a styrene–divinylbenzene chloromethylated copolymer is insufficiently high and therefore its replacement by an ionogenic group does not take place to completion.

Korshak *et al.* developed a method for obtaining bromo- and iodomethylated styrene-divinylbenzene copolymers: this involved the nucleophilic replacement of chlorine by bro-