COPOLYMERIZATION OF 3,4-EPOXYHEXAHYDROBENZYL ACRYLATE WITH VINYL MONOMERS*

S. Yu. Zaitsev, A. Ye. Batog, A. V. Bondarenko
and V. V. Zaitseva

M. V. Lomonosov State University, Moscow
Physico-organic and Carbon Chemistry Institute, Ukr. S.S.R. Academy of Sciences

The kinetics of the 3,4-epoxyhexahydrobenzyl acrylate (EHBA) copolymerization with acrylonitrile (AN), styrene (ST) and their azeotropic mixture in the presence of benzoyl peroxide (BP) at 333 and 348°K are described. Elemental analysis and IR-spectroscopy have been used to determine the composition of the resulting copolymers, the constants of the process and the chain units distribution. Under some conditions the epoxy group does not participate in the copolymerizations.

THE use of bifunctional monomers, especially of the epoxy acrylates, is of some theoretical and practical interest, as there is here the possibility of synthesizing polymeric materials with the desired crosslinking frequency.

The copolymerization of epoxy acrylates with vinyl monomers by a radical mechanism could be expected to yield linear polymers containing reactive epoxy groups in the branches and to give rise to ring-opening under some conditions with crosslinking. This would make it possible to trace and study the mechanism of formation of crosslinked copolymers. However, one first has to study the reactivity of the vinyl group present in 3,4-epoxyhexahydrobenzyl acrylate (EHBA) in its copolymerization with some standard vinyl monomer, and this was the aim of the work reported here.

EXPERIMENTAL

The EHBA was produced by reacting equimolar quantities of tetrahydrobenzyl alcohol with acrylic acid; this was followed by epoxidation of the intermediate product with peracetic acid. The previously purified product was vacuum-distilled and the fraction coming over a 341–342°K/3 hPa was collected. The EHBA used in the copolymerization had $d_4^{25} = 1.0730$ g/cm³, $n_D^{25} = 1.4793$, epoxide number 23.0%, $M = 181.7$ (ebullioscopic).

The inhibitor (hydroquinone) was removed from the ST and AN, also other impurities, by repeated washing with a 10% alkali solution at a 1 : 1 ratio and then with water until neutral. The product was dried over anhydrous CaCl₂ for 2–3 days. The dry monomers were distilled and the fractions with b.p. = 331°K/4 hPa (ST) and 351·8°K (AN) was collected. The purities of these monomers were 99·7 and 99·5% respectively. The BP was purified

by double reprecipitation with methanol from its chloroform solution. Its purity after vacuum-drying was 99·85% (iodometric).

The EHBA copolymerization with either AN or ST, or with their azeotropic mixture was a bulk process and the temperature 333 and 348°K. The BP was used as 0·001 mole/mole of the mixture. The % conversion to the polymer was determined by dilatometry. The calculated monomers and BP quantities were weighed at 0·001 g precision, were mechanically mixed until all of the BP had dissolved and the mixture was placed in a standardized dilatometer. The solution was degassed, the dilatometers sealed, weighed and placed into an oven in which the temperature was kept within $\pm 27°$K of that required. The dilatometer was removed from the oven at some time interval, was rapidly cooled and a special attachment then used to extract the mixture from the interior. The polymer solution was diluted with chloroform (to an about 1% polymer content) and was precipitated with anal. grade methanol. The precipitate was vacuum-dried to constant weight at room temperature and its quantity g used to calculated constant K (the contraction factor) in the equation: $g = \Delta V/K$ [1], in which ΔV—shrinkage of the system during polymerization.

TALBE 1. VALUE K AS A FUNCTION OF THE COMPOSITION OF THE INITIAL MONOMERS MIXTURE FOR THE RADICAL COPOLYMERIZATION WITH BP AT 333°K

Monomers, molar ratio		ΔV	g, g	K, g^{-1}
ST : EHBA	(ST+AN)$_N$: EHBA			
0 : 1·0	—	—	—	0·0970*
0·2 : 0·8	—	0·140	1·3526	0·1109
0·4 : 0·6	—	0·180	1·4229	0·1265
0·5 : 0·5	—	0·240	1·7924	0·1339
0·6 : 0·4	—	0·175	0·2411	0·1410
0·8 : 0·2	—	0·110	0·7074	0·1555
1·0 : 0	—	—	—	0·1704*
—	0·2 : 0·8	0·135	1·0861	0·1243
—	0·4 : 0·6	0·145	0·9646	0·1505
—	0·5 : 0·5	0·168	1·0256	0·1638
—	0·6 : 0·4	0·068	0·3844	0·1769
—	0·8 : 0·2	0·215	1·0591	0·2030
—	1·0 : 0	—	—	0·2295*

* Found by extrapolation.

The copolymer composition was determined by IR-spectroscopy, elemental analysis [2], and from the epoxy-groups content of the copolymer. The quantitative IR-analysis made use of 0·015 g/ml chloroform solutions which were poured into 1·00 to 0·11 mm thick NaCl tubes. The standard curve was produced from the measurement results of the components concentrations and their nitrogen, epoxy groups contents as well as the optical intensities of the 1728 cm^{-1} (C=O, EHBA) and 2238 cm^{-1} absorption lines (C≡N, AN). The number of ST chain units was determined from the difference. The proportionality factors for the respective chain units were: $K_{ST} = 0·00247$, $K_{AN} = 0·00598$, and $K_{EHBA} = 0·0236$ (1/mole %).

The turbidimetric titrations of the copolymer solutions were made at 298°K in a FET instrument; the stirring speed was 125 rpm and the original concentration 0·1 g/100 ml solvent. An acetone–methanol mixture was used as the solvent–precipitant system [3]; the viscosity of the copolymers was determined at 303°K in MEK [4].

The reactivities of the terminal vinyl groups of the epoxy acrylates were studied in the EHBA copolymerization with AN, ST or the azeotropic mixture of the last two. The kinetic parameters of the process, using binary and ternary systems, were calculated from the experimental shrinkage factor (Table 1).

RESULTS

The factor K decrease is a linear function of the EHBA content increase in the original monomers mixture. The K-values were used to determine the conversion S at various concentration ratios of the monomers; $S \leqslant 25\%$ for the two-component systems and $\leqslant 15\%$ of the 3-components ones. S was a linear function of time τ (Fig. 1).
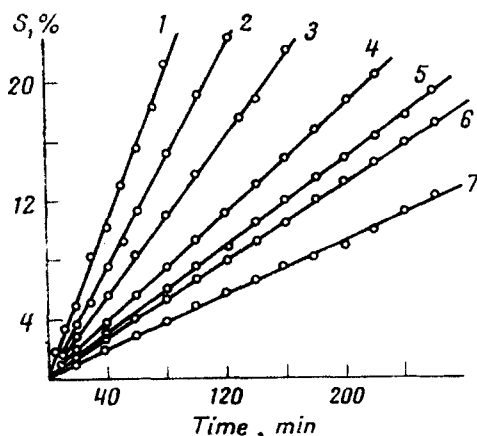

FIG. 1   FIG. 2

FIG. 1. Conversion of the monomers mixtures as a function of time using 0·001 mole BP/mole mixture at (°K): 1—348, 2-7—333 and various ratios; molar fractions: 1—0·7 : 0·3 AN : : EHBA, 2—0·2 : 0·8 (ST+AN)_N : EHBA, 3—0·2 : 0·8 ST : EHBA, 4—0·4 : 0·6, 5—0·5 : : 0·5, 6—0·6 : 0·4, 7—0·8 : 0·2.
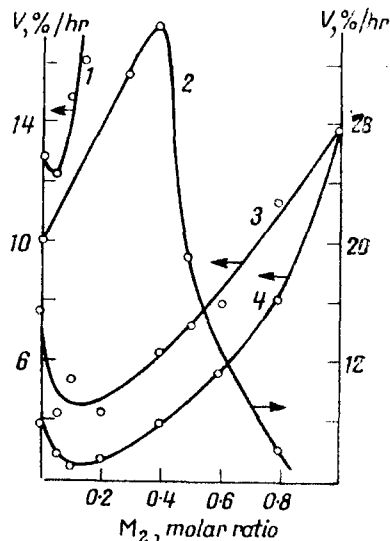
FIG. 2. The copolymerization rate as a function of the monomers composition. 1—(AN +ST)_N : EHBA, 2—AN : EHBA, 3—(AN+ST)_N : EHBA, 4—ST : EHBA, Temp., °K: 1, 2—348, 3, 4—333.

The process rate calculated from the slope of the lines shown in Fig. 1 increased with the EHBA content of the monomer mixture when ST–EHBA was used (Fig. 2). The rate–composition curves passed through a minimum at a 10–20 mole % EHBA content, after which they ascended slightly (Fig. 2, curves 3, 4). This type of change of the total rate can be explained by the differing reactivities of the monomers and the radicals formation. The rate curve for AN–EHBA (Fig. 2, curve 2) passes through a peak at 40 mole % EHBA and then drops when

the EHBA content increased. This rate change can be assumed to be associated with the effect of the AN...EHBA donor–acceptor complexes; their presence must increase the ratio at which the monomers alternate in the copolymer chain.

Raising the temperature from 333 to 348°K increased the rate for the 3-components system by a factor of about 5 (Fig. 2, curves *1, 3*). This is quite understandable on remembering that such a temperature increase will increase the number of reactive centres.

The products were copolymers and not homopolymer mixtures as indicated by the turbidimetric titration of their solutions with the acetone–methanol system (Fig. 3a). The sedimentation boundary γ shifted to larger values on increasing the EHBA content in the monomers mixture, i.e. the mol.wt. of the products dropped (Fig. 3a, curves *2–4*) and the copolymer had the most homogeneous mol.wt. at a 15 mole % EHBA content (curve *3*). The intrinsic viscosities of the terpolymers (ST–AN–EHBA) change in parallel with the reaction rate. The

TABLE 2. THE COPOLYMER COMPOSITIONS AS A FUNCTION OF THE INITIAL MONOMERS COMPOSITION AND THE CONVERSION

([PB] = 0·001 mole/mole mixtare, 333°K)

Monomers content, mole %				S, %	Copolymer composition, mole %			Epoxy value, %	
ST	(ST+AN)_N	AN	EHBA		ST	AN	EHBA	found	calculated
—	—	70·0	30·0	3·4	—	58·2*	41·8	—	9·61
—	—	60·0	40·0	3·8	—	52·9*	47·0	10·51	10·81
—	—	—	—	6·9	—	54·0*	46·0	10·65	10·58
—	—	50·0	50·0	2·2	—	45·9*	54·1	—	12·44
—	—	—	—	9·2	—	44·1*	55·9	12·70	12·85
—	—	20·0	80·0	0·7	—	29·7*	70·3	—	—
80·0	—	—	20·0	15·2	57·8	—	42·2†	9·71	—
60·0	—	—	40·0	15·0	42·8	—	57·2†	13·16	—
50·0	—	—	50·0	20·5	25·6	—	71·8†	16·51	—
40·0	—	—	60·0	15·6	23·8	—	76·2†	17·53	—
20·0	—	—	80·0	15·9	10·5	—	89·2‡	20·52	—
—	95·0	—	5·0	3·5	58·4	33·8	5·6‡	—	—
—	—	—	—	5·7	55·1	37·0	6·2‡	—	—
—	—	—	—	7·0	56·1	37·8	6·0‡	1·68	1·38
—	90·0	—	10·0	3·7	54·2	31·2	12·6‡	—	—
—	—	—	—	6·7	52·5	33·7	12·7‡	—	—
—	85·0	—	15·0	3·8	53·3	31·5	17·3‡	—	—
—	—	—	—	7·1	51·0	31·0	18·4‡	—	—
—	80·0	—	20·0	4·6	—	—	25·8†	5·93	—
—	50·0	—	50·0	15·1	—	—	47·6†	10·94	—
—	20·0	—	80·0	12·4	—	—	65·6†	15·08	—

* Determined from the nitrogen content.
† Calculated from the epoxy groups quantity.
‡ Determined by IR spectroscopy.

[η]-monomer mixture composition curve passes through a peak at a 5 mole % EHBA content (Fig. 3b) which points to a maximum entry of EHBA into the copolymer composition.

The EHBA present in the co- and ter-polymers (Table 2) becomes larger as its proportion increases in the monomers mixture. There is no change of the epoxy groups content in the initial process stages. It was thus clear that the copolymerizations of epoxy acrylates with vinyl monomers will yield linear copolymers with reactive epoxy groups. The copolymerization constants for the system AN(M_1)–EHBA were calculated for the known copolymer compositions (Table 2) by the method described by Ezrileyev and co-workers [5]: $r_1 = 0.30 \pm 0.03$, $r_2 = 0.41 \pm 0.04$, $r_1r_2 = 0.123$; for the ST(M_1)–EHBA system they were: $r_1 = 0.24 \pm 0.10$, $r_2 = 2.12 \pm 0.24$, $r_1r_2 = 0.59$.

This means that the growing radicals (AN–EHBA system) more rapidly add on to "foreign" monomer molecules than to their "own". The growing radicals addition will be more rapid to AN than to EHBA because r_2 is slightly larger than r_1. This is in good agreement with the total rate of copolymerization

FIG. 3   FIG. 4
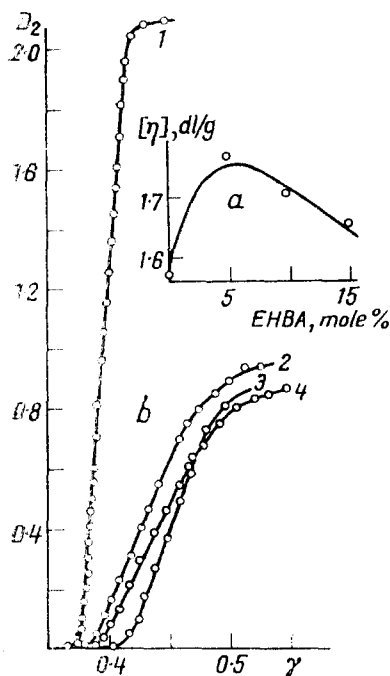
FIG. 3. The intrinsic viscosity as a function of a—the EHBA content of the terpolymer, b—the turbidimetric titration curves for 333°K and various monomer ratios, mole %: 1—61.7 : 38.3 ST : AN, 2—95.0 : 5.0, 3—85.0 : 15.0, 4—90.0 : 10.0 of (ST+AN)ₙ : EHBA.
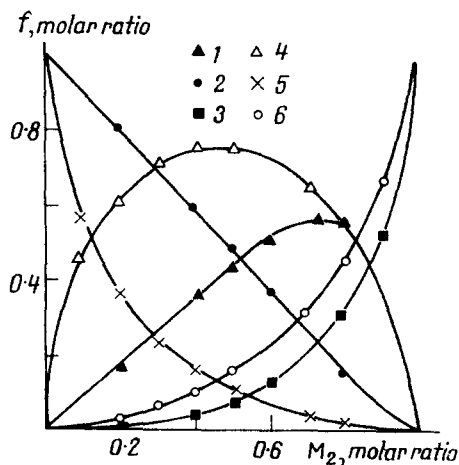
FIG. 4. The units distribution in the macromolecular chains of: 1-3—ST–EHBA, 4-6—AN–EHBA copolymers; 1, 4—M_1M_2, 2, 5—M_1M_1, 3, 6—M_2M_2.

(Fig. 2, curve *2*), which decreases as the EHBA content increases in the original monomers mixture. The product forming in the initial process stages contains an almost equal number of AN and EHBA chain units (Table 2). This system has an azeotropic point at a 46 : 54 mole % AN : EHBA ratio.

The growing radicals add on more rapidly to the EHBA molecules when ST is one of the monomers; this results in an enrichment of the copolymer macro-molecules with EHBA chain units even when an AN excess is present in the initial mixture of monomers (Table 2). The curve of the total process rate passes through a minimum in this copolymerization system. A rate reduction at a larger ST content in the original mixture is probably connected with the larger reactivity of the growing radical which terminates in EHBA when compared with that terminating in ST.

The largest number of M_1M_2 diads=f, was found at a 54 : 46 mole % ratio in the case of AN : EHBA and at a 27 : 73 mole % ratio for ST : EHBA (Fig. 4). The peaks practically coincide for the total rate and distribution curves in the case of the AN : EHBA system and there is a large degree of alternation.

The findings thus indicate that the vinyl group present in EHBA is reactive enough to yield copolymers with vinyl monomers which incorporate the epoxy group in the macromolecular chain.

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