The electrical and magnetic properties have been studied. High-temperature vacuum ageing is found to reduce the electrical conductivity. Careful refinement from low-molecular weight impurities increases the conductivity.

REFERENCES

1 V. I NIKITINA, A. I. MAKLAKOV, R S. BALAKIREVA and A. N. PUDOVIK, Sb. Geterotsepn vysokomol soyed (Collection Heterochain Macromolecular Compounds) Izd Nauka, 87, 1964
2 I P. ZHURAVLEVA, E A ZGADZAI and A. I MAKLAKOV, Vysokomol soyed **6** 488, 1964
3 E A ZGADZAI and A I MAKLAKOV, Sb itogovoi nauchn konf KGU za 1963 (Proc of the Scientific Conference of the Kazan State University, 1963) (Exact Sciences) Kazan, 52, 1964
4 L BELLAMY, Infrared Spectra of Complex Molecules, Foreign Lit Pub. House, 1963
5 C N. R RAO, Elektronn spektry v khimii. (Electron Spectra in Chemistry) Izd Mir, 1964
6 I M KUSTANOVICH, I I PATALAKH and L S POLAK, Kinetika i kataliz 4, 167, 1963

COPOLYMERIZATION OF ACRYLONITRILE WITH BENZYL- AND TETRAHYDROFURYL ACRYLATES*

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COPOLYMERS based on acrylonitrile and the esters of α,β-unsaturated acids have been widely used as plastics, rubbers and chemical fibres A study of the properties of copolymers of a large number of these two-component systems has shown that polymeric materials fulfilling widely varying requirements can be synthesized.

The principal relations of the radical copolymerization of acrylonitrile with aliphatic esters of acrylic and methacrylic acids are now known, and data have been obtained on the relative reactivities of the monomers [1–4]

According to certain authors, the relative reactivity of the monomers of one homologous series depends mainly on the polarity of the molecules, and not on the size of the alkyl groups in the alcohol radicals (as in the case of the esters of unsaturated acids [5, 6]) But, as found by Tamikado and Iwakura, the activity

COPOLYMERIZATION CONSTANTS

AN(M_1)–ester (M_2)	Copolymerization constants			$\dfrac{1}{r_1}$	Q	e
	r_1	r_2	$r_1 \times r_2$			
BA	0 294±0 08	0 636±0 07	0 187	3 50	0 433	−0 09
BM	0 206±0 02	0 810±0 02	0 167	4 85	0 590	−0 13
TA	0 602±0 10	0 773±0 07	0 465	1 66	0 160	+0 32
TM	0 154±0 03	0 710±0 01	0 110	6 50	0 664	−0 28

of acrylates on copolymerization with acrylonitrile diminishes as the size of the alcohol group increases [7] This seems to be because steric factors may hinder the copolymerization reaction

It is therefore very interesting to study the influence of the acrylate structure on its activity in copolymerization with acrylonitrile. We have therefore studied the copolymerization of acrylonitrile (AN) with benzyl and tetrahydrofural acrylates (BA and TA respectively) and methacrylates (BM and TM) in bulk in the presence of $1\ 22 \times 10^{-2}$ mole/l. azo-bis-isobutyronitrile at 60° up to low stages of conversion.

The copolymerization constants of the monomers were determined graphically using the Mayo and Lewis differential composition equation [8] (Table).

The relative activities of the ester monomers with respect to the radical AN ($1/r_1$) show that the methacrylates have greater activity than the acrylates

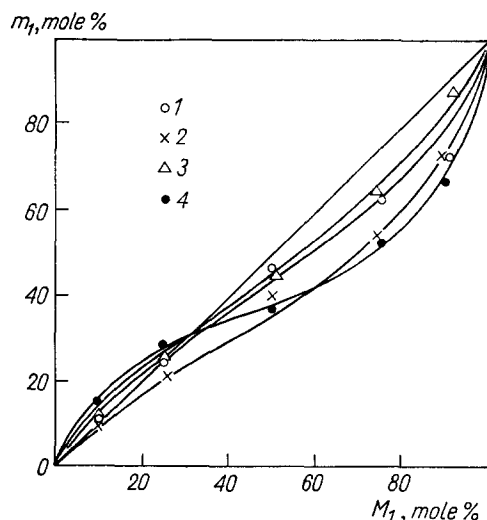As we can see from Fig 1, four pairs of monomers may form azeotropic mixtures with a low AN content

FIG 1 Composition of copolymers vs the initial monomer ratio 1—AN–BA, 2—AN–BM, 3—AN–TA, 4—AN–TM M_1—AN concentration of starting stock, m_1—AN concentration of copolymer

The constants Q and e, which reflect the specific activity (conjugation) of the monomers and their polarity, were determined by the Alfrey–Price method [8]·

$$r_1 = \frac{Q_1}{Q_2} \exp[-e_1(e_1-e_2)]$$

$$r_2 = \frac{Q_2}{Q_1} \exp[-e_2(e_2-e_1)]$$

where Q_1 and e_1 are the specific activity and polarity of AN, 0·6 and $+1·2$ respectively [1].

As we can see from the Table and the data in the review of [9], the polarity of benzyl and tetrahydrofuryl esters is approximately the same as that of the aliphatic acrylates and methacrylates with the same number of carbon atoms, although the former have higher activity in copolymerization with AN. Here, of course, the steric factors due to the large dimensions of the aliphatic groups are important. For instance, if the esters of phenyl and tetrahydrofuran rings are added to the molecule, the polarity of the monomers changes, which can be seen from the constants for the relative reactivities of benzyl and tetrahydrofuryl acrylates and methacrylates.

The products of the copolymerization constants of the monomers of each pair are low, indicating that the monomers have a great tendency to alternation. The common regularity of vinyl monomers can be seen from the Q and e values; when a methyl group appears at the double bond e falls and Q rises [8].
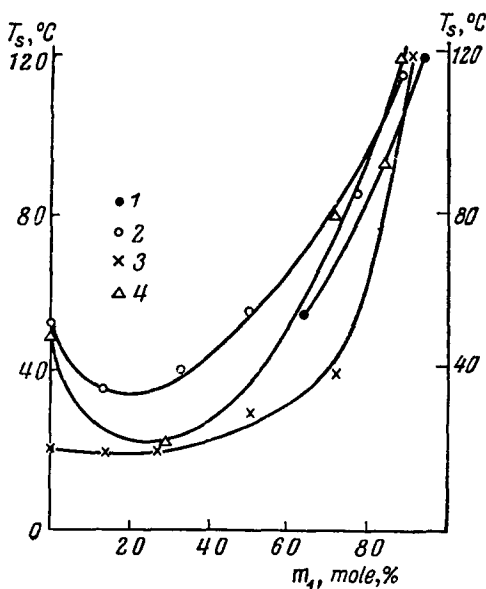

FIG. 2. Softening point T_s vs. copolymer composition: 1—AN–BA, 2—AN–BM, 3—AN–TA, 4—AN–TM. m_1—AN concentration of copolymer.

As the ester component fraction of the copolymers increases so does their solubility; their softening point falls, which can be seen from Fig. 2. It can be seen from the thermomechanical curves that at 70–80% ester concentration the softening point is at a minimum, but copolymers containing up to 80–90% acrylonitrile units have quite high softening points. Thus copolymers with a large AN content are quite suitable for making synthetic fibres, which has been demonstrated by moulding fibres by the water–dimethylformamide method.

EXPERIMENTAL

The starting esters were prepared as described in [10]. A high degree of monomer purity was established by IR spectral analysis and thin-film chromatography After standard purifying treatment AN had m p. 76°/728 mm, n_D^{20} 1 3905, d_4^{20} 0 810. The copolymerization was carried out in ampoules, the air dissolved by the monomers was removed by repeated freezing and thawing in an argon flow. The copolymers were reprecipitated in water from dimethylformamide, dried to constant weight and analysed for nitrogen content, using the Kjeldahl method. The compositions were calculated from the formula

$$m_1 = \frac{A\ N\ 100}{1400 + N\,(A - B)}$$

where m_1 is the molar fraction of AN in the copolymers, %; B, A are the molecular weights of the monomers; N—the nitrogen content, %.

The thermomechanical curves were taken on a Kargin dynamometer balance with specimens which had been produced by press-moulding powders.

CONCLUSIONS

(1) The bulk copolymerization of acrylonitrile with benzyl and tetrahydrofuryl acrylates and methacrylates has been performed in the presence of azo-bis-isobutyronitrile.

(2) The copolymerization constants of these esters have been determined, and their polarities and specific activities found. The thermomechanical properties have been studied.

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REFERENCES

1 The Chemistry of Acrylonitrile, New York, 1951
2 P. FRAM, G. T. STEWART and A. J. SZLACHTUN, Ind and Eng Chem 47. 1000, 1955
3 J. MILLER, Chem Listy 48 1591, 1954
4. A. S. NAIR and M. S. MUTHANA, Makromolek. Chem. 47: 138, 1961
5 C. S. MARVELL and R. SCHWEN, J. Amer. Chem. Soc. 79 6003, 1957
6 C H. BAMFORD, A. D. JENKINS and E. F. WHITE, J. Polymer, Sci. 34: 271, 1958
7. T. TAMICADO and Y. IWAKURA, J. Polymer Sci. 36. 530, 1959
8 T. ALFREY, D. BORER and G. MARK, Copolymerization, Foreign Lit Pub House, 1953
9. L. J. YOUNG, J. Polymer Sci. 54: 411, 1961
10 M. A. ASKAROV and A. S. BANK, Sb. Fizika i khimia prirodnykh i sintetichesklkh polimerov. (Collection Physics and Chemistry of Natural and Synthetic Polymers.) 1, 172, 1962