EFFECT OF THE MEDIUM ON THE HOMOGENEOUS RADICAL COPOLYMERIZATION OF UNSATURATED CARBOXYLIC ACIDS WITH VINYL MONOMERS*

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THE copolymerization of methacrylic acid with vinyl monomers in solvents capable of forming hydrogen bonds has been used as a model to demonstrate, in principle, the possibility of regulating the copolymer composition and the values of relative reactivity [1]. Since the publication of our first paper, a number of new reports has appeared in which it has been shown that the medium similarly affects the copolymerization of acrylic acid [2, 3], and the range of polymers which exert an effect on the reactivity of methacrylic or acrylic acid during copolymerization has been broadened [4]. In the present paper we shall report results obtained in our laboratory on the copolymerization of acrylic and methacrylic acids in specifically solvating solvents, and we shall also present information about the possibilities of obtaining copolymers of these acids with other monomers, the copolymers being homogeneous in composition at all stages of the reaction. We have previously reported on this method at the All-Union Scientific and Technical Conference, "Development of Scientific Research Work in the Field of Acrylates" in 1965.

EXPERIMENTAL

Methacrylic acid (MAA) and acrylic acid (AA) were frozen to remove water, and then purified by double fractional distillation *in vacuo*. The following fraction were selected: MAA, boiling point 72°C/20 mmHg, n_D^{20}, 1·4316; AA, b.p. 52°C/20 mmHg, n_D^{20}, 1·4220.

Methyl methacrylate (MAA) was dried with calcium hydride and purified by fractional distillation in argon at normal pressure; b.p. 100°C, n_D^{20}, 1·413.

Methylacrylate (MA) was dried with calcium chloride and distilled over calcium hydride; b.p. 80°C, n_D^{20}, 1·3984. Styrene (ST) was dried with phosphorus pentoxide and double-distilled under vacuum; b.p. 45°/20 mm, Hg n_D^{20} 1·5462.

Dimethylformamide (DMFA) was dried with potassium hydroxide and purified by vacuum distillation; boiling point, 41°C/20 mmHg.

The remaining reagents used in carrying out the experiments were dried and purified by the standard methods of preparative organic chemistry; their properties did not differ from the tabulated values. The copolymerization of the mixtures, from which atmospheric

oxygen was removed, was carried out at 25–75°C in special ampoule dilatometers. During the copolymerization of MMA–MAA, the initial mixtures which contained considerable quantities of MAA underwent heterophase polymerization. In the solvents used by us copolymerization took place homogeneously. Benzoyl peroxide (BP) and dicyclohexylperoxydicarbonate (DCC) were used as initiators, and were purified beforehand by recrystallization. Copolymerization was carried out to 5–7% conversion. The copolymer was then precipitated, purified by being reprecipitated three times, and brought to constant weight *in vacuo* at 55°C. Analysis of the copolymers was carried out by titration of the carboxyl groups either with an alcoholic alkaline solution in the presence of thymolphthalein, or conductometrically. The results from the conductometric titration and from the titration in the presence of thymolphthalein were in good agreement. The electrical conductivity of the solutions was determined on equipment connected in a bridge circuit fed from a ZG-10 generator at a frequency of 100 c/s. An oscillograph was used as the recording instrument.

RESULTS AND DISCUSSION

Figure 1 shows data about the effect of different solvents on the compositions of copolymers obtained from MMA–MAA and ST–MAA monomer mixtures. In the captions to these and all the subsequent Figures, the composition of the monomer mixtures and of the copolymers in expressed in mole fractions: M_2 is the mole fraction of AA or MAA in the monomer mixture, m_2 the mole fraction
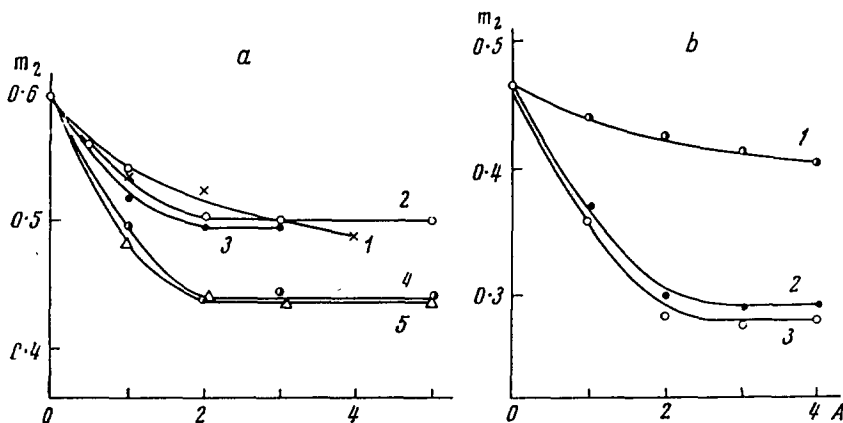

FIG. 1. Composition of the copolymer obtained with (*a*) an equimolar MMA–MAA mixture and (*b*) with a mixture 0·67 ST–0·33 MAA: dependence of solvent additions. Temperature, 45°C; [BP]=0·0082 mole/l.; m_2—mole fraction of MAA in the copolymer; *A*—molar ratio solvent : MAA. *a*: *1*—dioxane; *2*—ethylene glycol; *3*—ethanol; *4*—DMFA; *5*—pyridine; *b*: *1*—acetone; *2*—pyridine; *3*—DMFA.

of AA or MAA in the copolymer, and N the number of moles. In all cases, the MAA concentration in the copolymer specimens falls only to a definite limit. The additions may be placed in the following order of decreasing effectiveness of their action on copolymer composition: DMFA, pyridine, dioxane, alcohols, acetone. The molecules of these substances have atoms and groups capable of forming

hydrogen bonds with MAA and AA. A distinguishing feature of this effect is that it is not very sensitive to polymerization temperature. The appropriate data are shown in Fig. 2, from which it may be seen that the characteristics of the curves remain almost unaltered as the temperature is raised to 75–90°C.
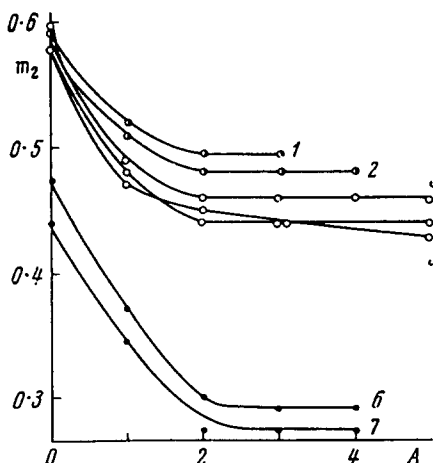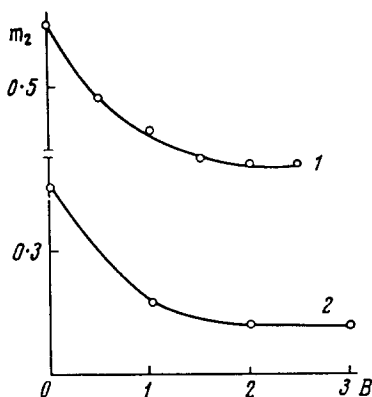

FIG. 2.   FIG. 3.

FIG. 2. Dependence of the copolymer composition on the amount of solvent at various temperatures: 1–5—0.5 MMA–0.5 MAA; 1—ethanol, [BP]=0.0206 mole/l., 45°C; 2—ethanol, [BP]=0.0041 mole/l., 75°C; 3—DMFA, [DCC]=0.0175 mole/l., 25°C; 4—DMFA, [BP]= 0.0206 mole/l., 45°C; 5—DMFA, [BP]=0.0041 mole/l., 75°C; 6—0.67 ST–0.33 MAA, pyridine, [BP]=0.0206 mole/l., 45°C; 7—0.67 ST–0.33 MAA, pyridine, [BP]=0.002 mole/l., 90°C; m_2 is the mole fraction of MAA in the copolymer; A is the molar ratio of solvent : MAA.

FIG. 3. Composition of the copolymer obtained from a mixture of 1—0.5 MA–0.5 AA, 2— 0.75 ST–0.25 AA; dependence on the concentration of DMFA, 55°C; [BP]=0.0082 mole/l.; m_2—mole fraction of AA in polymer; B—molar ratio DMFA : AA.

DMFA, as one of the most effective solvents influencing copolymer composition, was selected for a more detailed study. The data shown in Fig. 3 indicate that DMFA is an effective regulator of composition for both AA–MA and AA–ST copolymers. As in the case of MAA copolymers, DMFA has an effect on the copolymer composition when introduced in quantities not exceeding 2 moles per mole of AA. The composition curves for MMA–MAA, ST–MAA, MA–AA and ST–AA copolymers were therefore recorded with a two-fold excess of DMFA with respect to the unsaturated acid. Composition curves for these copolymers in bulk were obtained for comparison. The results are shown graphically in Figs. 4 and 5. The relative reactivities were calculated by the Mayo–Lewis differential method from the composition data, and then the parameters Q and e for the unsaturated acids for copolymerization in bulk and in DMFA were calculated from the latter. The calculation was carried out graphically by means of the Alfrey–Price equation for the Q–e scheme. The values obtained for r_1, r_2, Q and e are shown in the Table.

It may be seen from the Table that the reactivities of MAA and AA are less in a DMFA medium, and this appears as a reduction in their concentration in the copolymer over a wide range of compositions of the initial monomer mixture. Thus, as a rule, r_1 is increased and r_2 reduced (M_2 is MAA or AA). Data
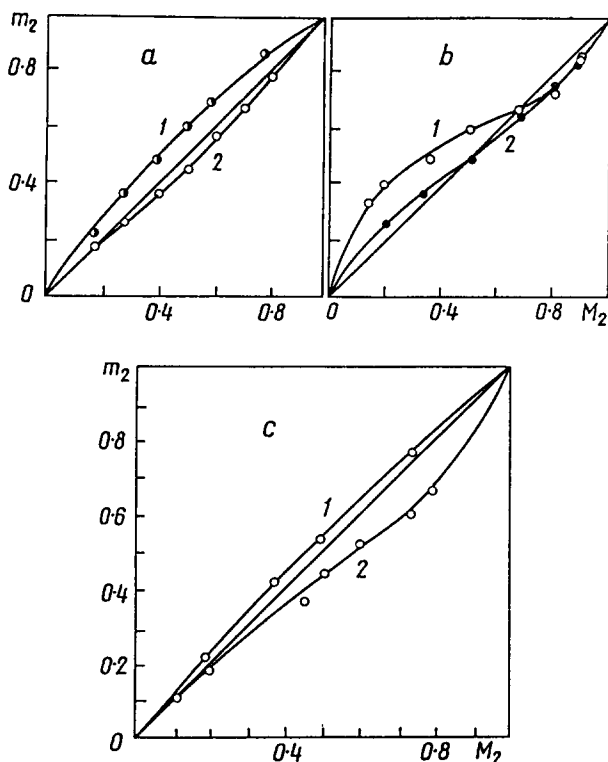

FIG. 4. Curves for the composition of the following copolymers: a—MMA-MAA; b—ST-MAA; c—MA-AA, 45°C; [BP]=0·0206 mole/l.; 1—in bulk; 2—at the following molar ratios: (a) and (b) DMFA : MAA = 2, (c) DMFA : AA = 2. In (a) and (b), M_2 refers to MAA, and in (c) M_2 refers to AA.

about the change in $r_1 = k_{11}/k_{12}$ represent the most valuable information. In fact, if it is assumed that DMFA forms hydrogen bonds only with AA or with MAA (but not with MMA, MA or ST), then it may be considered that DMFA has no effect on the value of k_{11}. The changes in the quantity r_1 may then be directly related to the change in k_{12}. The fact that in all cases r_1 is greater for copolymerization in DMFA than for the process in bulk is evidence that k_{12} becomes smaller under these conditions. This indicates directly that in a medium consisting of an agent capable of forming hydrogen bonds, unsaturated acids have a lower reaction capacity in reactions involving addition to macroradicals of MMA, MA and ST units.

The data in the Table give evidence of a reduction in the values of the parameters Q and e for MAA and AA during copolymerization in DMFA. The first points to a reduction in the ideal reactivity of unsaturated acids under these conditions and the second points to some lowering of the positive polarity of the double bond in unsaturated acids in DMFA.

It should be noted above all that the observed effects of a change in the reactivity of MAA and AA in polar solvents is clearly not connected with any potential capacity of these acids to dissociate. Figure 6 shows data about the electrical conductivity of MAA in DMFA, which is the most polar of the solvents used by us. The form of the curve shows that MAA is a weak electrolyte under these conditions. However, it follows from a comparison of the data in Fig. 6 with those in Figs. 1 and 2 that the copolymer composition remains unaltered after a two-fold excess of DMFA is reached, although the electrical conductivity continues to rise: this fact indicates a further increase in the degree of dissociation of MAA.

In our opinion, this is explained by a small number of dissociated MAA molecules, and this cannot be substantially reflected in the polymerization process.

It is known that carboxyl acids dimerize in the liquid state. This also takes place in the case of MAA and AA [5]. The dimers exist even if the acids are considerably diluted by inert solvents. In solvents capable of forming hydrogen bonds, the dimers break down and are replaced by acid–solvent complexes [6].
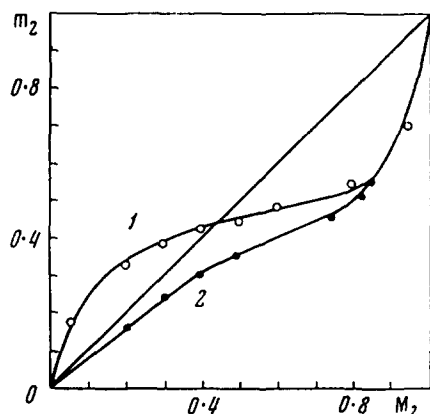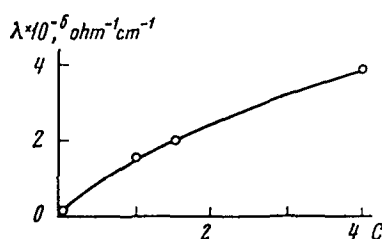

FIG. 5

FIG. 6

FIG. 5. Composition curves of ST–AA copolymer obtained at 45°C: [BP]=0·0206 mole/l.; 1—in bulk; 2—at a molar ratio DMFA : AA = 2; M_2 represents AA.

FIG. 6. Electrical conductivity of MAA in a mixture with DMFA at 25°C; c is the molar ratio DMFA : MAA.

With comparable proportions between the acid and solvents in the system, an equilibrium is set up. When applied to our case, one may write: $M_2 + 2S \rightleftarrows 2 MS$ (1), where M represents AA or MAA, and S is the solvent. It follows from the

results presented above that unsaturated acids in the dimerized form have a greater reactivity than the acid–solvent complexes. It is clear that the concentration range where the solvents affect the copolymer composition corresponds to the existence of both dimers and complexes. The curve for the change in

VALUES OF r_1 AND r_2 AND OF THE PARAMETERS Q AND e FOR MAA AND AA
UNDER VARIOUS CONDITIONS

(M_2 represents MAA or AA)

Conditions	Monomers	r_1	r_2	Q_2	e_2
In bulk	MMA–MAA	0.55 ± 0.02	1.55 ± 0.06	1.51	$+0.68$
	ST–MAA	0.2 ± 0.02	0.66 ± 0.08		
In DMFA	MMA–MAA	0.98 ± 0.04	0.68 ± 0.05	0.74	$+0.4$
	ST–MAA	0.53 ± 0.02	0.45 ± 0.06		
In bulk	MA–AA	0.95 ± 0.02	1.1 ± 0.06	0.70	$+1.1$
	ST–AA*	0.25 ± 0.02	0.05 ± 0.01		
In DMFA	MA–AA	0.98 ± 0.02	0.42 ± 0.02	0.15	$+0.45$
	ST–AA	1.1 ± 0.04	0.08 ± 0.03	.	

* The values obtained for r_1 and r_2 agree with data from [3].

copolymer composition as the amount of polar solvent is increased is as it were a mirror reflection of the process involving replacement of the dimers by complexes. The fact that the temperature does not exert any substantial effect on the trend of the composition–amount of solvent curves is evidence of the fact that the equilibrium in reaction (1) does not thereby undergo any considerable shift. In fact, the equilibrium constant (K) for the reversible reaction (1) may be written in the form
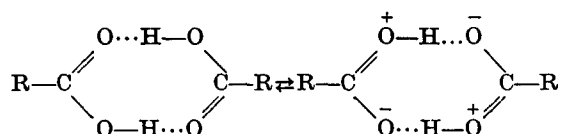
$$K = \frac{[MS]^2}{[S]^2 [M_2]} .$$

By using the expression $R \ln K = \Delta S - \dfrac{\Delta H}{T}$ for the equilibrium constant, we come to the conclusion that the effect of temperature on K is determined by the size of the enthalpy term. It follows from equation (1) that when the two hydrogen bonds in the dimer are broken, two hydrogen bonds between the acid and solvent are formed. The total energy of the hydrogen bond in the carboxyl acid dimer is 8–12 kcal/mole and the energy of ordinary hydrogen bonds is 3–5 kcal/mole [7]. Consequently, ΔH for reaction (1) is very small or approximately zero. This explains the fact that temperature has little effect on reaction (1), and because of this has little effect on the form of the composition–amount of solvent curves.

We suggest that the reason for the higher reactivity of the dimeric form of MAA and AA lies in the high resonance stabilization of the π-electron system in the dimer of the unsaturated acid or in the corresponding radical. Pauling has previ-

ously put forward a hypothesis [8] according to which additional stabilization involving the following resonance structures exists in the dimers of carboxylic acids:

$$R-C\underset{O-H\cdots O}{\overset{O\cdots H-O}{<}}C-R \rightleftarrows R-C\underset{\overset{-}{O}\cdots H-\overset{+}{O}}{\overset{\overset{+}{O}-H\cdots\overset{-}{O}}{<}}C-R$$

It is also possible to point to other factors favouring high stabilization of the electronic system of the dimer. It is known that the π-electrons of the carboxyl group which ends the system of conjugation may participate in hydrogen bond formation, the π-electron cloud thereby being to some extent transferred through the hydrogen bridge [9]. As a result of this there exists in carboxylic acids a certain delocalization of the π-electrons in the dimeric ring. In dimers of unsaturated carboxylic acids, the double bond is for this reason to a considerable extent conjugated with the π-electronic system of the substituent, and the unpaired electron in the corresponding radical is to a considerable extent delocalized. A confirmation of this suggestion is the fact that the parameter Q, which characterizes the degree of conjugation of the double bond with the substituent, is greater in the dimers of carboxylic acids than in the complexes between these acids and the solvent.

The reduction in the positive value of the parameter e for AA and MAA in complexes with DMFA is explained by further polarization of the O—H bond of the acids when the hydrogen bond is formed with DMFA. Because of this polarization the partial negative charge on the oxygen is increased, and this reduces the partial positive charge at the double bond because of the inductive effect.

Synthesis of MAA and AA copolymers which are uniform with respect to the composition of their fractions. Because of the non-uniform reactivity of monomers during copolymerization, the copolymer obtained at high degrees of conversion consists of fractions with different compositions. In certain cases the composition of the fractions is sufficiently different to cause mutual incompatibility [10]. In order to obtain copolymers uniform in composition the process is usually carried out to 10% conversion, or the depletion in the more reactive component is made good during the course of the reaction. The first method involves considerable over-consumption of the monomers, and the second does not give strict uniformity in the product.

We have suggested a chemical method of obtaining copolymers of MAA and AA, uniform with respect to the composition of their fractions with polymerization to any degree of conversion [2]. The method is based on regulating, as described above, the composition of copolymers of MAA and AA by additions of polar solvents.

The copolymerization of equimolecular mixtures of MMA–MAA and ST–MAA to high degrees of conversion was discussed as an example. By using the values

found for the relative reactivities, we calculated the "instantaneous" compositions of the copolymers and monomer mixtures at different degrees of conversion. The calculation was carried out by Kruze's analytical method [11] for the system ST–MAA, and for the system MMA–MAA by Skeist's graphical method [10]. The graphical method was used in the second case because MMA–MAA systems with a considerable concentration of MAA polymerize in a heterophase manner. This may influence the accuracy of the determination of the quantities r_1 and r_2, and as a consequence may affect the accuracy of calculations by Kruze's method.

By using the equation for the material balance of one of the components [10], the "overall" compositions at various degrees of conversion were calculated from the instantaneous compositions of the monomer mixtures. The calculated relationships between the instantaneous and overall copolymer compositions are shown by the solid lines in Fig. 7. The points corresponding to the experimentally determined values of overall composition are also shown in Fig. 7.
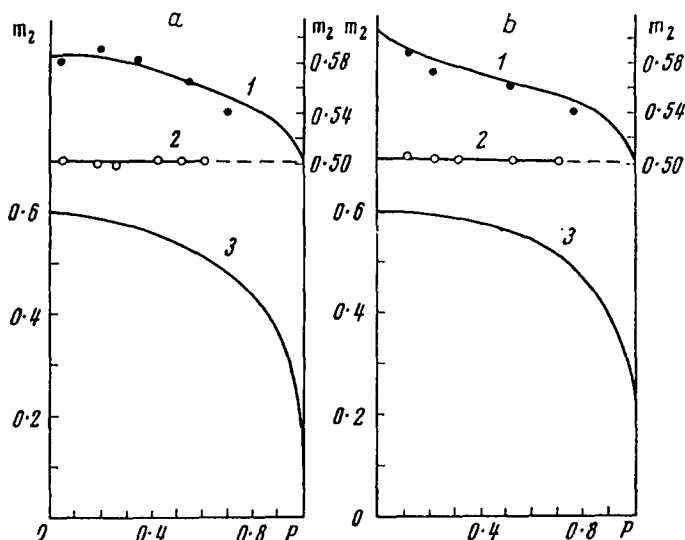

FIG. 7. Dependence of (3) the instantaneous and (1, 2) the overall composition of the following copolymers on the extent of polymerization: a—MMA–MAA; b—ST–MAA; 1 and 3 calculated curves. Experimental points: ● —copolymerization in bulk, [BP] = 0·0206 mole/l., 45°C; ○ —molar ratio DMFA : MAA = 0·9, [BP] = 0·0206 mole/l., 45°C. $P = [M]_0 - [M]/[M]_0$.

It follows from the data shown that the calculated values of overall composition agree satisfactorily with the experimental data (some discrepancy in the initial stages of the copolymerization of MMA and MAA is probably connected with its heterophase character). The curves for the instantaneous composition make it possible to conclude that in the final stages of copolymerization (starting from 60% conversion) a copolymer is formed which differs considerably in composition from the product formed in the initial stages.

In order to obtain MAA copolymer of constant composition at all stages of the process we used the possibility of regulating the copolymer composition as described in the first part of this paper. It is to be expected that if a quantity of solvent is taken such that, in its presence, a copolymer will be formed similar in composition to the initial monomer mixture, then at all stages of copolymerization the composition of the copolymer will be the same and equal to the composition of the initial mixture. For the copolymerization of equimolecular MMA–MAA mixtures in the presence of 0·9 mole of DMFA per mole of MAA, and also for the copolymerization of equimolecular ST–MAA mixtures in the presence of 1·1 mole of DMFA per mole of MAA, equimolecular MMA–MAA and ST–MAA copolymers are formed in the initial stages. These mixtures were polymerized to high degrees of conversion, and the overall copolymer composition was determined at various stages. It may be seen from the data in Fig. 7 that a copolymer of the same composition, equal to the composition of the initial mixture, is formed at all stages of the process.

The method discussed may be used for a variety of monomer mixtures where the possibility exists of regulating the monomer reactivity by changing the reaction medium.

CONCLUSIONS

(1) The copolymer composition and the values of relative reactivities during the copolymerization of methacrylic and acrylic acids with methyl methacrylate and styrene may be regulated by additions of solvents capable of forming hydrogen bonds with the acids. The effectiveness of this action is almost temperature-independent.

(2) A method has been developed for obtaining copolymers of methacrylic acid with fractions uniform in composition, the polymerization being carried out to any desired degree of conversion.

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THE RHEOLOGICAL PROPERTIES OF POLYDISPERSE cis-POLYBUTADIENES*

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THE study of the relationship of the rheological properties of polymers with their molecular parameters is of great importance in the formulation of a general theory on viscoelastic properties, and in the synthesis of polymers with useful optical properties. As viscous flow causes a shift of the centre of gravity in a medium having similar properties to those of the individual macromolecules, one must expect the rheological properties of a particular polymer to be primarily determined by the geometrical (dimensions, mol.wt.) and statistical (mol.wt. distribution (MWD), type of branching) parameters of its macromolecules.

The influence of the mol.wt. and of branching on the rheological properties of some elastomers has been recently examined by Kraus and coworkers [1–3], and by Vinogradov *et al.* [4]. Little has been done about the polydispersity and its effect on such properties.

The aim of the work reported here was to study the rheological behaviour of cis-polybutadienes (cis-PB) with different degrees of polydispersity in the presence of small, medium and large shear stresses σ and shear rates γ, equivalent to spontaneous cold flow of the polymers ($\gamma \simeq 10^{-3}$ sec^{-1}), during the evaluation of viscoelastic properties ($\dot{\gamma} \simeq 1$ sec^{-1}), and during processing ($\gamma > 20$ sec^{-1}).

EXPERIMENTAL

Several cis-PB sample series were studied (rubber SKD); these had been produced over a catalytic system based on titanium salts [5]. The cis-1,4 bond content in all the samples was 88–92%.