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The Liquid Crystalline State Copolymerization†

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Abstract—Mixtures of *p*-cetyloxybenzoic acid, *p*-methacrylyloxybenzoic acid (M_1) and styrene (M_2) exist in the liquid crystalline state over a relatively wide range of temperatures and compositions.

Copolymerization of M_1 and M_2 in the liquid crystalline state and dioxane and dimethyl formamide (DMF) solution was studied. Tert-butyl peroxide was used as initiator at a polymerization temperature of 105 °C. The copolymerization rate in the liquid crystalline state considerably exceeds that in the liquid phase. The molecular weight of copolymer formed in the liquid crystalline state is about 3–4 times higher than for copolymer formed in the liquid phase. The monomer reactivity ratios for the liquid crystalline state copolymerization are equal to $r_1 = 1.24$, $r_2 = 0.32$ and differ from the corresponding values for the liquid phase copolymerization ($r_1 = 0.84$, $r_2 = 0.13$ in DMF solution).

The value of $r_1 > 1$ in the liquid crystalline state copolymerization may be accounted for by the existence of mobile monomer (M_1) arrays in liquid crystal layers. The mechanism of copolymer formation in the liquid crystalline state is discussed.

Introduction

In the course of free radical copolymerization, the copolymer composition depends on the reactivity of monomers and their concentration in the initial monomer feed. For solid state copolymerization, the monomer reactivity ratios to a great extent depend on the parameters of the crystalline cell rather than the monomer reactivity itself. First, the rigidity of the crystalline cell should influence both the kinetic mobility of monomer molecules and the thermodynamic probability of chain propagation.

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Second, the mutual order of the monomer units in the crystalline lattice also influences the structure of resulting polymer, which can be a " replica " of the crystalline cell. In other words, the micro-uniformity of the monomer crystals should cause the formation of copolymer units with corresponding unit length similar to block copolymerization. However, no cases of forming block copolymer during solid state reactions are known. In eutectic mixtures, copolymer is formed with the same " stoichiometric " composition, as the initial monomer feed(1,2,3), but in uneutectic mixtures considerable portions of homopolymers are formed.(1,2)

Probably the definite conditions for the preparation of block copolymer can be realized during the liquid crystalline state copolymerization.

The wide set of mobile organized monomer arrays (M_1, M_1, M_1, M_1) is realized by mixing of the liquid crystalline (M_1) monomer with the liquid monomer (M_2) or solvent. This should lead to the formation of block copolymer, or at least, to considerable variations of the monomer distribution into polymer chains and kinetics of copolymerization.

Copolymerization of *p*-methacrylyloxybenzoic acid (MAOBA) with styrene was studied in the liquid crystalline state and in DMF and dioxane solutions. In a previous paper(4) it was shown that the mixture of *p*-cetyloxybenzoic acid (COBA) and MAOBA exists in the liquid crystalline state in the interval 78–136 °C. The liquid crystalline state is realized also in the wide range of temperatures and compositions by adding of the various organic solvents (and in particular second comonomer styrene) to the mixture of COBA and MAOBA.

Experimental

COBA and MAOBA were prepared as described in a previous paper.(4) Styrene and solvents were purified by conventional methods(5) and were chromatographically pure.

The copolymerization was carried out in 20 ml ampoules at 105 °C with 0.25% (mol) tert-butyl peroxide and 0.06% (mol) photo-inhibitor-amylnitrite ($C_5H_{11}ONO$). The total monomer concentration in the feed was 2.76 mol/l.

MAOBA and COBA were charged into the ampoule and evacuated to 10^{-4} mm. Hg. Styrene, initiator and inhibitor were condensed into this ampoule and sealed. A photoinhibitor was added to prevent the polymer formation during the fusion of the liquid crystal components at high temperature. The ampoule was placed into a transparent silicone oil bath and irradiated by UV-light at 150 °C. The reaction mixture was melted into the clear solution in 1–3 min. The ampoule was thermostated into the silcone bath at 105 °C, and the reaction mixture was cooled to the liquid crystalline state. The reaction was initiated immediately after stopping UV-irradiation. It was found that the photoinhibitor in the absence of UV-light does not influence the kinetics of the copolymerization. After the copolymerization, the reaction mixture was dissolved in dioxane and precipitated in a mixture of ether and light petroleum. The copolymers were filtered, dissolved in dioxane and reprecipitated in light petroleum. The copolymer composition was determined by the elemental analysis. The monomer reactivity ratios r_1 and r_2 were computed by the nonlinear least square method.(6)

The copolymers MAOBA–styrene were converted into copolymers methylmethacrylate–styrene by basic hydrolysis in methanol–dioxane solution and methylation with diazomethane.(7) The NMR study of the converted copolymers was carried out with a Varian MA-60/DA-60 spectrometer at 80 °C in CCl_4 solution.

Results and Discussion

The orientation of monomers in the liquid crystalline state influences to a great extent copolymerization reaction. The reaction rate in the liquid crystalline state considerably exceeds that in isotropic solution. The kinetic curves of the copolymerization in the liquid crystal and dioxane and DMF solution are shown in Figs. 1–3. It was found that the copolymerization rate depends on the initial monomer feed composition and decreases with decreasing of MAOBA concentration (Fig. 4). However, this dependence for liquid crystalline state is greater than that for the isotropic phase. On varying MAOBA : styrene ratio from 0.25 up to 4 the copolymerization rate in solution increases 5 times, but the reaction rate in the liquid crystal increased 16 times. This considerable increasing

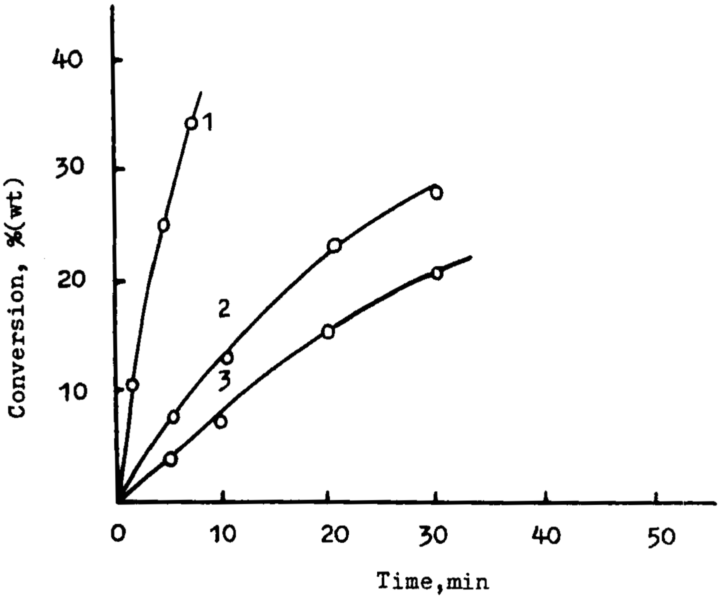

Figure 1. Kinetic curves of copolymerization MAOBA with styrene in different solvents at initial monomer feed 8:2. 1—COBA; 2—dioxane; 3—DMF.

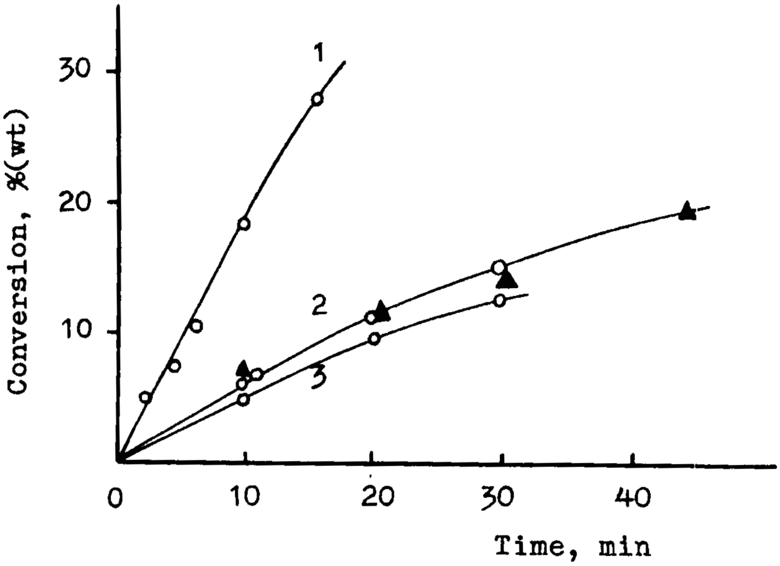

Figure 2. Kinetic curves of copolymerization of MAOBA with styrene in different solvents at initial monomer feed 1:1. 1—COBA; 2—dioxane; 3—DMF; ▲—acetic acid.

of the reaction rate is connected mainly with the increasing of the number of the mobile organized monomer arrays of MAOBA in the liquid crystalline phase. The probable structure of the such mobile organized monomer arrays was discussed earlier.(7)

The molecular weight of the copolymer formed in the liquid crystal (the intrinsic viscosity $[\eta] = 1.4$) exceeds that formed in liquid phase ($[\eta] = 0.76$). It is interesting to note that the copolymerization rate in dioxane for all runs exceeds that in DMF (Figs. 1–4). This fact takes place because dioxane is a " poor " solvent for MAOBA(7) and its copolymers as compared with DMF.

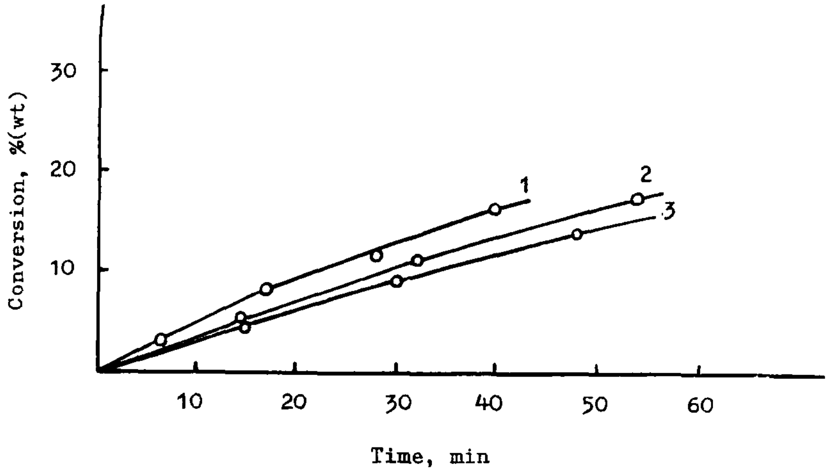

Figure 3. Kinetic curves of copolymerization of MAOBA with styrene at different solvents at initial monomer feed 2:8. 1—COBA; 2—dioxane; 3—DMF.

In a " poor " solvent macromolecules shrink and active species are screened by the segments of macromolecules. It leads to the loss of the mobility of active species, and consequently, the bimolecular termination reaction decreased.

But the high copolymerization rate in the liquid crystalline solvent COBA is caused by structure of mesomorphic state only, since the rate of copolymerization in such a closely related non-mesomorphic solvent as acetic acid is much lower (Fig. 2).

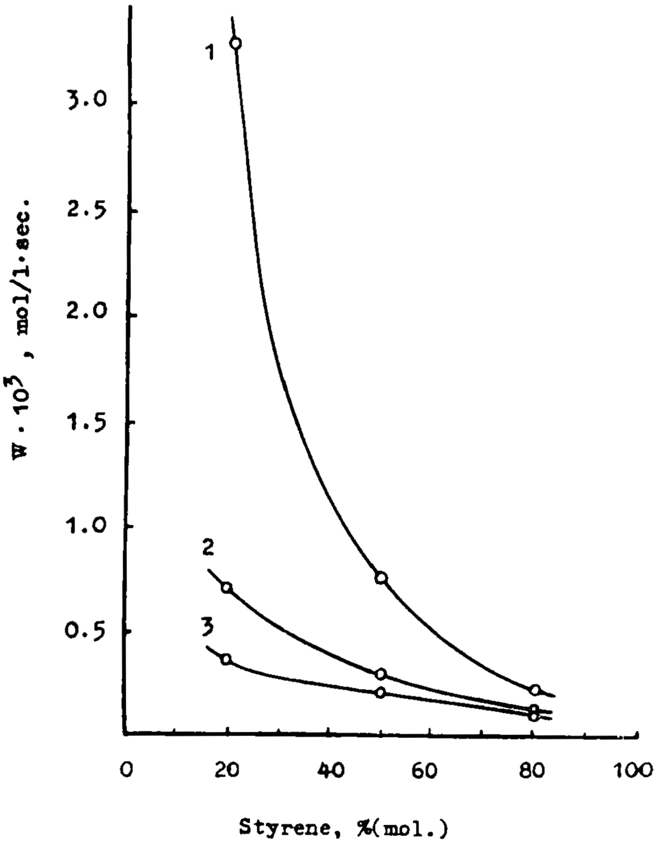

Figure 4. Dependence of copolymerization rate on initial monomer feed composition in different solvents. 1—COBA; 2—dioxane; 3—DMF.

The liquid crystalline state of the comonomers influences the composition and the distribution of monomer units in the copolymer. The monomer reactivity ratios r_1 and r_2 and calculated values of Q and e, which characterize the reactivity of comonomers, are collected in Table 1. However the present methods of the determination of r_1 and r_2 are not true in the case of liquid crystalline state copolymerization, because the concept " average concentration " for mesomorphic mixture loses its physical meaning as will be shown later. Therefore the values of r_1 and r_2, calculated from the assumption about a constancy of the local concentration throughout the whole reaction volume in the reaction medium are abstract, though to some extent it reflects the structure effects. In solution the monomers (MAOBA) and styrene show a trend to form the alternate copolymer ($r_1 < 1$, $r_2 < 1$), but in the liquid crystal the MAOBA macroradical reacts mainly with own monomer ($r_1 > 1$).

TABLE 1 The monomer reactivity ratios of MAOBA (M_1) and styrene† (M_2) and Q and e for different phases and solvents

Solvent	r_1	r_2	Q_1	e_1
COBA (Liquid crystal)	1.24	0.32	1.46	0.17
Dioxane (isotropic)	0.85	0.21	1.68	0.51
DMF (isotropic)	0.84	0.13	2.40	0.70

† For styrene were accepted $Q = 1.0$, $e = -0.80$

The copolymers formed in the liquid crystalline state are not true block copolymers, though some trend to form short blocks is observed. The NMR-spectrum of copolymer MMA-styrene obtained from copolymer MAOBA-styrene by the analogous reaction is shown in Fig. 5. This sample was prepared by copolymerization in the liquid crystal at initial monomer feed composition MAOBA : styrene 8 : 2. Three peaks X, Y and Z from $-OCH_3$ centered groups with the chemical shift 6.27τ, 6.85τ and 7.37τ are observed.

It was shown earlier⁽⁸⁾ that the peak Z corresponded to triads of the SMS-type, i.e. the single units of MAOBA within polymer chain. This peak must be absent if only copolymer with block length > 1 is formed.

As shown in Table 1, the calculated values Q and e characterizing the comonomers reactivities are changed considerably in the course of liquid crystalline state copolymerization as compared with the liquid phase process. Of course these values lose any physical meaning on the same reasons as calculated values r_1 and r_2.

The high reaction rate and the changing of copolymer composition in the course of the liquid crystalline state copolymerization may be understood from consideration of the liquid crystalline structure.

It is well known there are two alternative theories of liquid crystalline structure. According to swarm theory, the liquid crystals consist of discrete swarms, containing about 10^4–10^5 molecules in

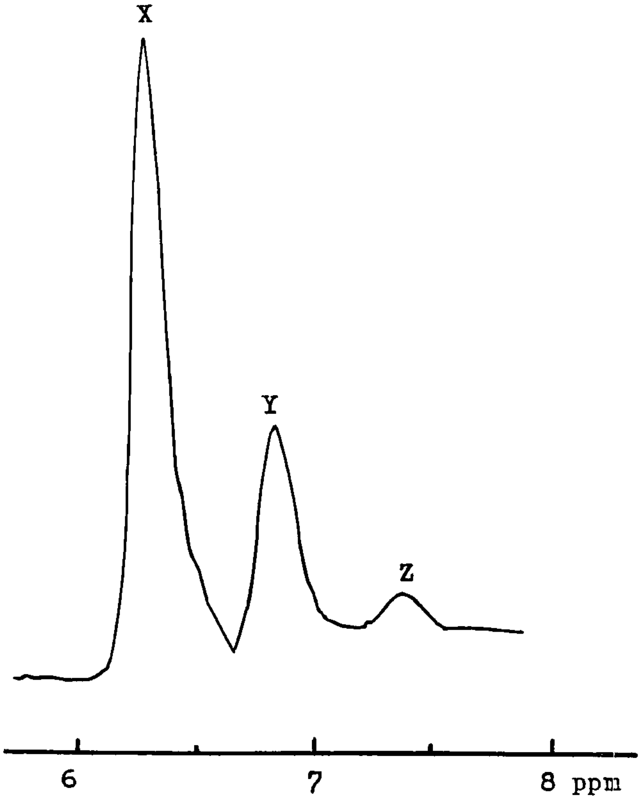

Figure 5. NMR spectrum (60 mc) of copolymer 8:2 in CCl_4 at 85°.

each. But many experimental data show that this theory is not suitable for description of mesomorphic structure. Particularly the formation of short sequences of MAOBA in copolymer in the course of liquid crystalline copolymerization also rejects the existence of large discrete swarms.

However we can not accept another theory describing the liquid crystal as a continuum with a continuous changing of orientation of molecules.

Really even in the isotropic liquids with small intermolecular interaction there are different kinds of fluctuations (density, orientation, concentration). The nature of fluctuation formation was shown by Smoluchowski and Einstein.(9,10) The probability of existing of any kind of fluctuation is determined by equation

$$W = \exp([S' - S]/k)$$

where k—Boltzmann constant,

S—entropy of the most probable state (but not only one),

S'—entropy of the probable state with fluctuations.

According to Frenkel,(11) the probability of the heterophase fluctuation may be determined from equation

$$W_h = C \exp\left[\frac{\Delta H(T - T_0)}{T \cdot T_0}\right]$$

where ΔH—thermal effect of phase transition,

C—constant,

T—temperature of the sample,

T_0—temperature of phase transition.

It is obvious that in the comparatively wide temperature range near the phase transition liquid crystal–isotropic liquid, the probability of the existence of heterophase fluctuations is high, since ΔH is small.

In the liquid crystal, heterophase fluctuations exist as isotropic microdrops, and in the pretransition state (above the phase transition temperature liquid crystal–isotropic liquid) they exist as mesomorphic clusters.

The phenomena of heterophase fluctuations over a wide temperature range were proved directly by Tsvetkov *et al.*(12)

Thus we can consider the liquid crystalline state as a mesomorphic state with defects and distortions appearing owing to heterophase fluctuations.

As has been shown,(13,14) the growth of chain molecules is the fast process both in oriented media (crystal state) and in the course of phase transitions.

Therefore the high rate of copolymerization in the liquid crystalline state might be explained by the favored orientation of monomer molecules in the liquid crystalline layers.

Another reason for this fact is the existence of heterophase fluctuation during an infinitely long time. We can consider the continuous generation and disappearance of fluctuations as the micrological phase transition promoting growth of chain molecules.

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