Study of Phase-Diagram and Copolymerization of *p*-Ethoxy-*p*'-acryloyloxy-azobenzene with Cholesteryl Acrylate*

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ABSTRACT: The effect of the mesomorphic (cholesteric) state on the chemical reactivity was investigated by the copolymerization reactions of *p*-ethoxy-*p*'-acryloyloxyazobenzene (EOA) and cholesteryl acrylate (CA). The monomers form partially miscible solid solutions on the EOA side. The eutectics having minimum clearing point values are cholesteric solution at a CA content of 0.3 M. Polymerization rates in the cholesteric state are generally lower than those in the isotropic liquid at a given temperature. Relative reactivity ratios of the copolymerization are as follows: $r_{CA,1}=0.28$, $r_{CA,m}=0.16$, $r_{EOA,1}=0.57$, and $r_{EOA,m}=1.10$. Products of the corresponding constants refer to statistical copolymerization. Differences in monomer polarizability are high ($\Delta\epsilon=1.32$) as calculated from the r values. In the mesomorphic state, the probability of incorporation of CA into the chain is less, compared to the isotropic state.

KEY WORDS Cholesteryl Acrylate / Azo-Acrylate / Liquid Crystal / Phase Diagram / X-ray Diffraction / Copolymerization / Reaction Abilities / Quantum Chemistry /

It is supposed in the kinetic treatment of a liquid-phase copolymerization that the uniform distribution of monomer molecules leads to a statistical reaction.¹ In ordered systems, this supposition is quite unreasonable. In the overwhelming majority of solid-state copolymerizations, comonomers form eutectics,² and thus, the connection between the monomers A and B takes place mainly on the crystalline interface within the eutectics. Formation of block copolymers is expected. In the copolymerization of acrylonitrile with acrylic acid,³ acrylonitrile blocks were actually detected by an intramolecular cyclization reaction. In other cases, however, random copolymers were produced due presumably to altered phase conditions caused by the appearance of the copolymer.^{4,5}

The mesomorphic systems represent intermediates between the isotropic liquids and completely ordered crystalline states. In the mesomorphic lattice, the molecules are more easily inter-

changeable and preconditions of isomorphism are less strict⁶ than in the crystalline state.⁷ Under the inevitable conditions of the statistical monomer distribution and the phase homogeneity, the effects of order on the reaction can be studied most favourably in the liquid crystalline state.

Copolymerizations in the liquid crystalline state have usually been investigated only qualitatively. Compositions of copolymers as functions of the monomer ratios are however, not reported. From *p*-methyl-*p*-acryloyloxyazobenzene (MAAB) and cholesterylvinyl succinate (CVS), identical copolymer compositions were obtained both in the cholesteric and in the isotropic liquid states.⁸ Melting points of the copolymers gave minimum in a certain range of the composition. Homopolymers of MAAB and CVS were found nematic⁹ and smectic,¹⁰ respectively. Kinetic constants of homopolymerization of CVS were slightly altered by changing the isotropic liquid state into cholesteric. On the other hand, molecular mass of the polymer formed in the cholesteric state was higher than that produced in the isotropic liquid state.^{5,11}

* Polymerization in Liquid Crystals X. Part IX.: cf. ref 5.

In the present paper, effects of the state of copolymerization on the structure of the copolymer are studied in the systems *p*-ethoxy-*p*'-acryloyloxyazobenzene (EOA) and cholesteryl acrylate (CA). Lecoin *et al.*¹² obtained insoluble polymers from the homopolymerization of EOA initiated by UV light both in isotropic liquid and in the nematic state. More details on the reaction are not available. Homopolymerizations of CA in the smectic state were reported by us^{13,14} and independently by Tobolsky *et al.*¹⁵ and by De Visser *et al.*¹⁶ Phase modifications of CA were disputed since the modification of CA stable at ambient temperature could be either smectic or crystalline depending on the purity of the monomer.¹⁷

EXPERIMENTAL

Monomers were synthesized as described previously.^{13,18} The melting point of CA was 125.6°C, that of EOA was 105°C, the clearing point of the latter was 142°C, in agreement with literature data.¹² Melting and clearing points were determined by a Zeiss Polmi A polarization microscope using Boetzius-type thermostated plate. Heating rate around the phase transition was 0.5 to 1°C min⁻¹.

Monomer/monomer phase diagrams were determined by polarization microscopy, DSC-2b, and X-ray diffractometry as reported previously in detail.^{5,8-11}

Copolymerization were carried out in the mesomorphous and isotropic liquid states at 118°C by initiation of 0.5 per cent of *t*-butyl perbenzoate. The initial mesomorphic system was transformed into the isotropic liquid state by the addition of 30% of monochlorobenzene at 118°C. It was found for the homopolymerization of CVS that such an amount of a neutral solvent had no appreciable influence on the kinetic constants.¹⁰ After a reaction period of 1–10 hours, the polymerizing system was dissolved in chlorobenzene containing *p*-hydroquinone. The product of polymerization in the isotropic state was soluble in chloroform, while that formed in the mesomorphic state was insoluble. The polymer was

precipitated from chlorobenzene by acetone. Reaction times established so that the conversion would be 10–15%. Systems polymerizing in the mesomorphic state became turbid and the precipitated copolymers were hardly soluble. During the polymerizations of systems of higher EOA content, the reaction mixture was not completely dissolved in chlorobenzene, leaving a gelous swollen fraction.

The composition of the copolymers was determined by nitrogen microanalysis.

Copolymers were agitated with dimethyl formamide in order to extract any possible poly(EOA). The residue was dissolved in a 3:2 (v/v) acetone/dichloroethane mixture for separation from the incidental poly(CA). In any case, no homopolymer was detected by analysis of the solutions. Thus, the polymer phase was regarded homogeneous throughout the reaction time.

RESULTS AND DISCUSSION

DSC and polarized light flux curves of EOA/CA monomer–monomer system are presented in Figure

Figure 1. DSC and depolarization light flux curves of ROA/CA systems. Denotations in the Figure were used for preparation of the monomer/monomer phase diagram. Specimen contains 50 vol% of EOA.

Figure 2. Ratio of the eutectic melting heat to the over-all melting heat for EOA/CA systems plotted against the composition.

Figure 3. Schematic pattern of X-ray diffractograms recorded at 25°C with EOA/CA systems as a function of the composition.

1. The characteristic changes used for preparation of the phase diagram are denoted. In Figure 2, the ratio of the area under the DSC peak marked by ΔH to the overall enthalpy change is plotted against the composition. It can be seen in the Figure that the eutectic composition¹⁹ is 0.3 M CA/0.7 M EOA. Figure 3 illustrates schematically the X-ray diffractograms recorded at 20°C. EOA was subjected to a phase transition into its second modification¹² by the influence of CA, as apparent in the phase diagram. On the side of CA, the location and intensity of reflexion peaks change up to the EOA content of 0.2 M. X-ray diffractogram of CA is poor in reflexions. Related literature is contradictory in regard to the phase conditions of CA.¹⁷ X-ray diffractograms were thus recorded at several compositions as a function of temperature by a Guiner camera of 2R radius using CuK_α radiation monochromatized by crystal. These recordings are presented in Figures 4 and 5 for CA and CA/EOA

systems of different compositions, respectively. Figure 4 includes the serial number of measurements since each recording enhanced the thermal loading of the sample by 2 hours and CA undergoes a thermal polymerization above 70°C.

The first recording in Figure 4 refers to a crystalline substance rich in reflections although the number of peaks was lower than usual for crystals containing similar molecules in size. At 115°C, the number of reflections decreased while at 120°C, the X-ray diffractogram was identical with that of a liquid. By recooling to 115°C, the pattern did not change and the sample proved to be cholesteric at both temperatures. By further cooling to 60, 40 and 26°C, CA structure appeared which was poor in reflections. This structure was also observed previously,^{13,14} and polymerizations were carried out in this system. Diffractogram recorded at 26°C for a sample heat for a longer period and containing a few per cent of polymer consisted of broadened

Figure 4. X-ray scattering of CA obtained in a Guinier camera as a function of temperature. The figures on the right side represent serial numbers of the experiment and are proportional to the dose of the X-ray initiating polymerization of CA.

Figure 5. X-ray scattering of EOA/CA mixtures of different composition recorded by a Guinier camera as a function of temperature.

Figure 6. Scanning electronmicrograph of a broken surface of a CA tablet. Magnification: 5800 $\times$.

Figure 7. X-ray diffractogram of EOA in the nematic state oriented by a magnetic field of 1.9 T at 400 K.

peaks corresponding to the smectic *G* structures.²⁰ This structure formed during the annealing of the monomer was stabilized by the polymer produced. The noncrystallinity of the material is evidenced by the scanning electronmicrograph in Figure 6.

An X-ray diffractogram of nematic EOA oriented in a magnetic field (1.9 T) is shown in Figure 7, which shows a cibotactic structure. In contrast to the conventional cibotactic model,^{21,22} reflections associated with the molecular length are not sharp. This recording is related to that of the oriented DNA²³ in many respects. A detailed analysis of this

Figure 8. Polarization micrographs of EOA/CA contact prepartes at different temperatures. Left hand side, pure EOA; right hand side, pure CA between; the concentration of CA is increasing from left to right.

diffractogram is beyond the scope of the present work but it should be noted that the diffuse blackenings indicated by arrows and the lesser blackening of the medial regions than that of the background cannot be explained by the cibotactic model which assumes a mosaic texture.

In X-ray diffractograms for EOA/CA systems of different compositions recorded at various temperatures, it can be appreciated (Figure 5) that, above 80°C, the initially crystalline eutectics have melted and only the diffraction peaks of the excessive component remain, depending on the composition. These reflections disappear as the temperature is elevated and above 100°C, only two diffuse spots persist characteristic to a cholesteric mixture. Around this temperature, a slight endothermic transition is indicated in the DSC recordings but cannot be detected in the X-ray diffractograms.

In the presence of EOA, due to its inhibiting effect, no polymer was formed by thermal initiation in CA. Figure 5 shows CA diffractograms poor in reflections throughout. Above 80°C, the diffractograms are poorer. At 85 to 115°C, systems containing no reciprocal lattice are formed depending on the composition. This change is caused by the melt-

Figure 9. Phase diagram of the EOA/CA system.

Figure 10. Polarization micrograph of the EOA/CA eutectics at 373 K. Magnification: $340\times$.

ing of eutectic crystals.

A micrograph of CA and EOA contact prepreparates are presented in Figure 8 as a function of temperature. The sample was heated and then cooled to 116°C followed by reheating. It is apparent that a multiphase system exists. On the EOA side, the structure is cholesteric while, on the CA side, a phase transition front proceeds toward CA as the temperature increases to 121°C . Melting of the cholesteric mixture does not start at CA but at an intermediate concentration and shifts toward EOA. The minimum curve of melting point is characteristic of a limited miscibility system.

Figure 9 illustrates the phase diagram obtained by a collection of the experimental data of the above investigation. The two components form partially miscible solid solutions between 0 and 0.2 M of the EOA content. CA containing 0.2 M EOA form eutectics with EOA at an EOA concentration of 0.75 M and has a melting point of 80°C . The molten

Figure 11. Polymerization rate of EOA/CA mixtures in (%/h) as a function of the composition and the phase state: Temperature, 395 K ; $\circ$, isotropic liquid state; ∇ , cholesteric state.

eutectic system is cholesteric. At $105\text{--}108^{\circ}\text{C}$, texture of the very opaque melt changes with a slight thermal effect into a transparent birefringent phase. This transition cannot be observed in contact prepreparates. According to the X-ray diffractograms and the pictures on the texture, CA forms the S_C phase even in the eutectics and the molten eutectic system has a cholesteric structure as illustrated by the micrograph in Figure 10. Both CA and EOA are dissolved in the cholesteric melt. At 118°C a one-phase cholesteric (N^*) system is present at any composition. Polymerization experiments were carried out at this temperature.

An exact interpretation of the changes in the cholesteric system at 100 to 114°C cannot be given. A photoisomerization (*trans* to *cis*) known for azo compounds²⁴ should take place to some extent. This, however, is in contradistinction with the DSC curves where a small enthalpy change occurs at this temperature.

The rate of copolymerization is abruptly reduced by increasing the amount of EOA. Assuming a linear kinetic course, a logarithm of reaction rate (in % per hours) is plotted against the composition in Figure 11. In the isotropic liquid phase, the log

Figure 12. EOA content of copolymers formed in EOA/CA mixtures of different compositions as a function of EOA content of the initial monomer mixture and of phase state: $\circ$, isotropic liquid; $\square$, cholesteric state.

Figure 13. Calculation of copolymerization constants by the linearization procedure of Tüdös and Kelen: $\circ$, isotropic liquid; $\square$, cholesteric state $\alpha=1$.

reaction rate decreases proportional to the EOA content. In the mesomorphic state, the reaction rate is almost invariant in the range of 0.2 to 0.7 M of EOA but sharply decreases both below and above these concentrations. Between 0.6 and 0.8 M of EOA content, the reaction rate is identical to that observed in the isotropic liquid but otherwise, is lower. The reaction rate in the nematic and cholesteric states was found to be lower in other cases, than that extrapolated to the same temperature for

the isotropic liquid state.^{8,10,25,26}

EOA content of copolymer products are plotted against the initial EOA comonomer content in Figure 12. In contrast to the MAAB/CVS copolymers studied previously,⁸ the present processes are different in the isotropic and cholesteric phases. Copolymerization constants were calculated by linearization of differential concentrations, using the method of Finemann and Ross²⁸ modified by Tüdös and Kelen²⁷ as shown in Figure 13. The copolymerization constants are as follows:

$$\begin{aligned} r_{\text{EOA},i} &= 0.55 & r_{\text{EOA},m} &= 1.10 \\ r_{\text{CA},i} &= 0.28 & r_{\text{CA},m} &= 0.16 \end{aligned}$$

The reactivity ratios depend on the phase state. Its value for EOA in the mesomorphic state is twice of the corresponding value obtained in the isotropic state. In the case of CA it is reversed. Since the rate of homopolymerization is lower in the mesomorphic than in the isotropic state, the enhanced reactivity ratio refers to a highly reduced probability of the $-\text{EOA} \cdot + \text{CA}$ reaction.

The product of the two reactivity ratios is far from the unity, reflecting unequivocally to statistical copolymer. Substituting this value into the equation of $Q-e$ scheme,²⁹ the difference between the e values of polarizability is 1.32 in either phase. Disparity in the two acrylates is unreasonably high. Assuming the validity of the $Q-e$ scheme, the phase dependence shows influence of order of molecules on the reactivity ratios of the monomers what is assumed to be a molecular parameter.

The present copolymers were found to be essentially soluble in contrast to the observation of Lecoin *et al.*¹² Their solubilities are, however, lower when formed in the mesomorphic state than those of products prepared in the isotropic state. This can be attributed only partially to the higher EOA content of polymers produced in the mesomorphic state; it is much more probable that the molecular mass of the copolymers is enhanced as in the case of corresponding azoxy compounds.¹¹

In conclusion, it may be said that the polymerization of EOA with CA leads to statistical copolymers. The mesomorphic state decreases the reaction rate in mixtures rich either in EOA or in CA. This diminution is slight if at all at intermediate compositions. In the mesomorphic state, however, the difference in monomer polarizability is less which

reduces the incorporation probability of CA. The EOA/CA system is different from the MAAB/CVS system inasmuch as its copolymer does not alter the phase state of the monomers and thus, the effect of the mesomorphic state on the reactivity ratios can be well observed. On the other hand, the *cis-trans* isomerism of the azo compound and its susceptibility to cross-linking due to the lability of azo bond are disturbing effects. It is certainly interesting that a compound, capable of acting as an inhibitor can be subjected to polymerization and copolymerization.

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