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Polymerization of a Nematic Liquid Crystal Monomer†‡

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Abstract—The purpose of this study was to ascertain whether a single component liquid crystalline phase represents an ordered matrix in which topochemical control can be exercised in intermolecular reactions. A detailed kinetic study of the polymerization of the new nematic liquid crystal monomer *N*-(*p*-methoxy-*o*-hydroxy-benzylidene)-*p*-aminostyrene was conducted in the nematic and isotropic phases. In addition, the polymerization in the nematic phase was conducted in a magnetic field of 1300 Oe. In disagreement with previous reports on other liquid crystal systems, no significant effect on the rates of polymerization or the nature of the product appears to be associated with the existence of the nematic phase or the presence of a magnetic field during the reaction.

1. Introduction

As a result of the long-range order associated with liquid-crystalline phases, the possibility of topochemical control⁽¹⁾ affecting either the rates or the products of reactions in these phases was first recognized by Svedberg.⁽²⁾ He studied the rate of thermal decomposition of picric acid, pyrogallol, and trinitroresorcinol in the nematic phase of *p*-azoxyphenetole at 140°. Orientation by external magnetic fields of 1000–2260 Oe decreased the rate of the decomposition reactions in all three cases. At the nematic-isotropic transition temperature (165°) there was a sudden increase in rate of picric acid decomposition.

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The latter effect was interpreted as a rapid increase in diffusion rate at the transition temperature, and the former effect was discussed in terms of restrictions to the thermal vibrational modes of the solute molecules imposed by the magnetic field. Recently, Bacon and Brown⁽³⁾ have given a preliminary report of a study of the Claisen rearrangement in a nematic solvent, and attribute an increased reaction rate to stereoselective character of the nematic phase.

A logical extension of the concept of topochemical control is to polymerization reactions, and attempts to polymerize organic monomers in the solid state have a history dating back more than 30 years when trioxane crystals were first shown to polymerize and reflect the geometry of the parent crystal.⁽⁴⁾ Highly oriented polymers can be prepared without the need of mechanical drawing, and in some cases undesirable side reactions which might occur in the liquid state or at higher temperatures may be avoided.⁽⁵⁾ The liquid crystalline phase could similarly preserve the orientation of monomer units; to date, no definitive study of such a polymerization has been conducted. Sadron has summarized work on polymerizations in nematic- and smectic-type gels in which he reports "microdomains" of one polymer within a matrix of another.⁽⁶⁾ Herz⁽⁷⁾ has studied polymerization of alkali metal salts of *p*-styryl-11-undecanoic acid in aqueous solution where domains of polymer are also formed. Amerik and Krentsel⁽⁸⁾ performed radiation-induced polymerization of vinyl oleate in the solid, smectic and isotropic phases, and reported that the morphology of the polymer obtained depended markedly on the phase. Crystalline polymer was obtained in the solid and mesomorphic phase, but the polymer obtained in the isotropic phase was a viscous liquid. Amerik *et al.*⁽⁹⁾ also studied the polymerization of *p*-methacryloxybenzoic acid in a smectic liquid crystalline solvent, *p*-cetyloxybenzoic acid, comparing it with a different isotropic solvent (dimethylformamide) and claim significant differences in rate and molecular weight.

As criterion for this study, it was felt that a careful investigation of a single component system—a well-characterized monomer polymerizing in the nematic and isotropic phases—would allow a critical re-examination of the role of order in mesophases on chemical properties. The study of vinyl oleate discussed above is not definitive since it has been reported⁽¹⁰⁾ that there exist *at least* two mesophases

in vinyl oleate with quite different transition temperatures than those observed by Amerik and Krentsel.⁽⁸⁾ A group of vinyl liquid crystal monomers of the anil type were accordingly synthesized, and the polymerization of one such compound, N-(*p*-methoxy-*o*-hydroxybenzylidene)-*p*-aminostyrene (MHS), studied in detail.

The reactivity and structural stabilization of liquid crystalline anils is an interesting problem in and of itself, independent of the polymerization problem. At the beginning of this work, it was not clear whether the introduction of the *o*-hydroxy group would destroy the liquid crystalline properties of the compound, but it was found on model compounds that the thermal stability was enhanced and cleavage of the anil group was hindered.⁽¹¹⁾ The corresponding polymer obtained from N-(*p*-methoxybenzylidene)*p*-aminostyrene was insoluble and probably undergoes considerable cross-linking associated with such processes as dimerization or cleavage of the anil.

2. Experimental

SYNTHESIS OF LIQUID CRYSTAL MONOMERS

Two groups of compounds were prepared: the N-(*p*-alkoxybenzylidene)-*p*-aminostyrenes, and the N-(*p*-alkoxy-*o*-hydroxybenzylidene)-*p*-aminostyrenes. Preparation and properties of the former group have already been described in a preliminary communication.⁽¹²⁾ For the *o*-hydroxy substituted anils, the procedure is as follows. *p*-Methoxy-*o*-hydroxybenzaldehyde was prepared by the method of Zemlen *et al.*⁽¹³⁾ *p*-Octadecoxy-*o*-hydroxybenzaldehyde was prepared by refluxing 1-bromo-octadecane and 2,4-dihydroxybenzaldehyde in alcoholic KOH for 24 hours. The methoxy compound was subjected to two fractional distillations yielding a fraction boiling at 276–277° at 2 mm Hg. *Analysis:* Calc. C 76.94%, H 10.76%, Found C 77.01%, H 11.01%. The aldehyde is then coupled with *p*-aminostyrene in a controlled atmosphere box at room temperature in the presence of a trace of hydroquinone. Table 1 lists the properties of these latter two anils. The observed transition temperatures were determined both optically, by microscopic observation on a Mettler FP2 hot-stage under crossed polarizers, and calorimetrically with a Perkin-Elmer DSC-1B Differential Scanning Calorimeter.

TABLE I Properties of N-(*p*-alkoxy-*o*-hydroxybenzylidene)-*p*-aminostyrenes

<i>p</i> -Alkoxy group	Transition Temperatures °C		Mesophase Identity
	Solid-mesophase	Mesophase-liquid	
MeO	111	124	nematic
C ₁₈ H ₃₇ O	93.5	108	smectic

POLYMERIZATION KINETICS ON MHS

MHS was chosen for this study because of its ease of purification and the tractability of the resulting polymer. MHS was sublimed twice and thoroughly mixed in a ballmill with 0.1 mole % of twice recrystallized benzoyl peroxide. The monomer was transferred to pyrex ampoules which were evacuated to below 10^{-3} mm Hg for 24 hours. Argon gas was purged through the samples and pumped out several times before the samples were finally evacuated and sealed. Ampoules were held in either oil baths or solvent baths with temperature control to $\pm 0.1^\circ$. For the polymerization in a magnetic field, ampoules were placed in a jacketed cell, through which oil was circulated, which was mounted in the gap of a permanent magnet whose intensity at the center of the gap was 1300 Oe. At appropriate intervals ampoules were removed, and the mixture of monomer and polymer extracted with ether in a Soxhlet extractor for 24 hours. The remaining polymer was dried in high vacuum and weighed.

CHARACTERIZATION OF POLY-MHS

Molecular weights of the polymer were determined in benzene with a Hewlett-Packard Vapor Pressure Osmometer 302B on samples which were dissolved in dibromomethane, reprecipitated with ethanol, and dried thoroughly in high vacuum. Viscosity measurements were performed in Ubbelohde viscometers in benzene at 25° .

3. Results

The benzoyl peroxide initiated polymerization of MHS in the solid phase is very slow; no polymerization occurs at 81° for seven days, but polymerization does take place at 100° . It was decided to focus

exclusively on the nematic and isotropic phase reactions, and Table 2 summarizes the rate constants for the polymerization and the % error as obtained by utilizing a standard least squares program. Figure 1 presents typical kinetic data at 115°. Figure 2 is an Arrhenius plot of the data in both the nematic and isotropic phases.

TABLE 2 Rate Constant for Polymerizations in the Mesomorphic and Isotropic Phases of MHS Initiated by Benzoyl Peroxide (0.1 mole %)

Temp. °C	Phase	Ksec ⁻¹ × 10 ⁵	% Error
115	Nematic ^(a)	1.77 ± 0.23	13.00
115	Nematic ^(a)	1.74 ± 0.14	8.05
115	Nematic	1.58 ± 0.17	10.70
115	Nematic	1.63 ± 0.21	12.90
118	Nematic	2.17 ± 0.10	4.61
121	Nematic	2.95 ± 0.33	11.20
127	Isotropic	5.62 ± 0.29	5.17
127	Isotropic	5.87 ± 0.14	2.38
127	Isotropic	7.78 ± 0.86	11.02
133	Isotropic	11.40 ± 0.80	7.00
139	Isotropic	13.80 ± 1.52	11.00
139	Isotropic	12.20 ± 1.49	12.20

^(a) These two experiments were performed in a magnetic field of 1300 Oe.

Kinetic data were taken at three different temperatures in both the nematic and isotropic phases. Measurements were restricted to a time period ~ 30–120 minutes after immersion of the ampoule with polymer yields restricted to ~ 20% in the nematic phase and ~ 50% in the isotropic phases; higher % conversions led to phase separations. There is the possibility of some small amount of phase separation at lower yields as well, but it could not be detected visually.

The results indicate that first order kinetics are followed in both phases. Calculating *separate* activation energies for the mesomorphic and isotropic phases gives values of 30.1 ± 0.8 and 21.3 ± 3.7 Kcal mole⁻¹ respectively. Calculating an activation energy for all data in *both* phases gives a value of 31.1 ± 3.0 Kcal mole⁻¹. Within the accuracy of the experiment, one cannot conclude that there is any significant change in the energy of activation or discontinuity in the rates of reaction at the nematic-isotropic transition temperature.

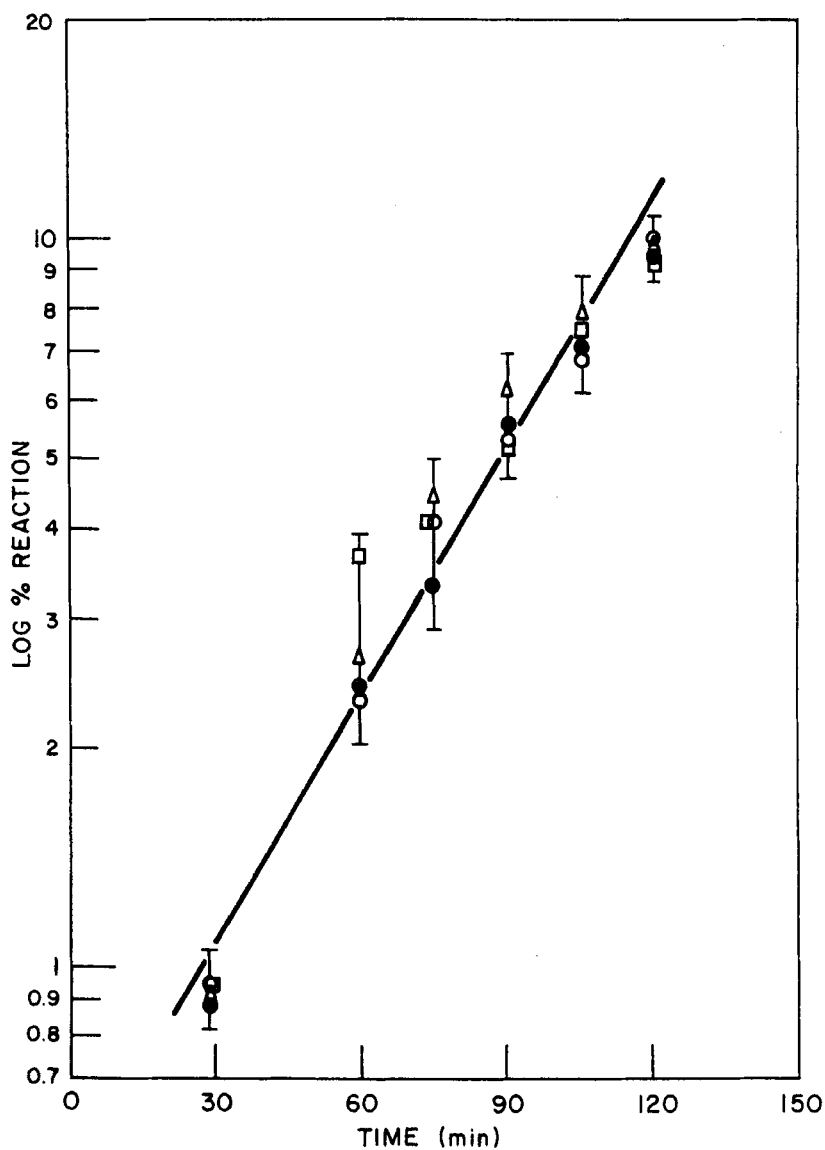


Figure 1. Log % reaction vs. time (minutes) for the formation of Poly-MHS at 115° (nematic phase). Two of the four runs were performed in a 1300 Oe magnetic field.

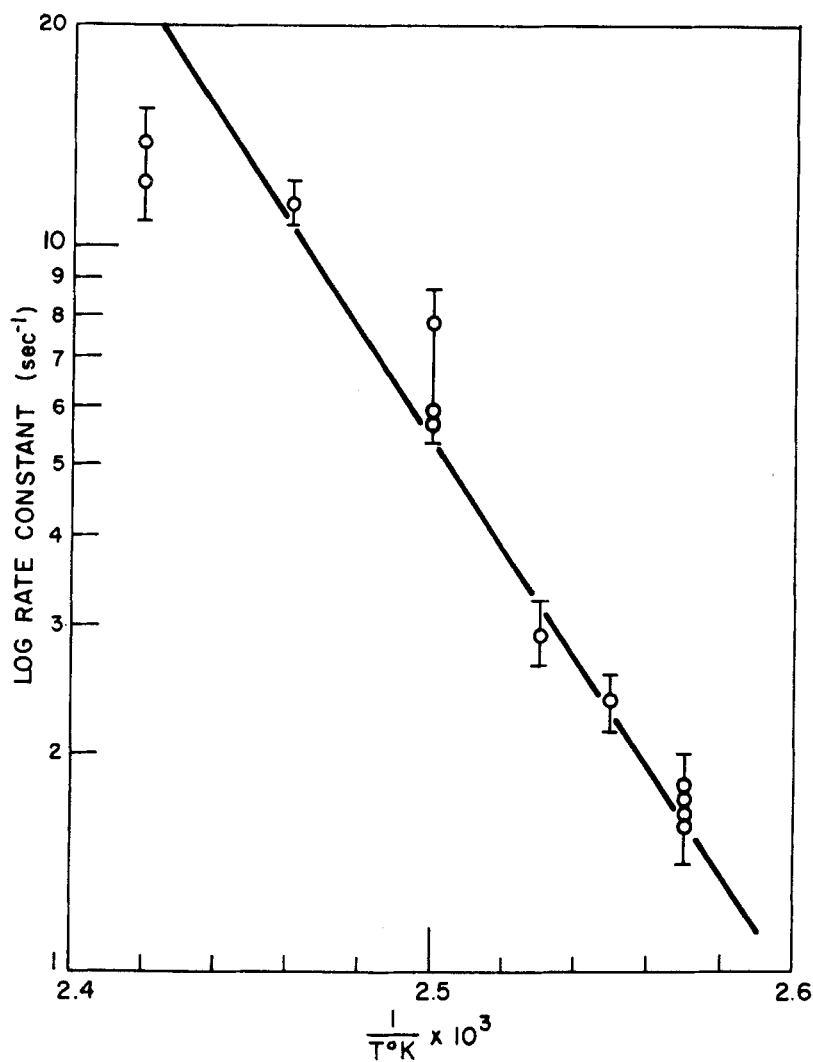


Figure 2. Arrhenius plot of polymerization of MHS in the mesomorphic and isotropic phases.

Polymer characterization studies further confirm that no significant difference exists in the nature of the resulting polymer. Table 3 lists the number average molecular weights of poly-MHS in different phases. Viscosity measurements and solubility tests also indicate no significant differences in the polymers obtained.

TABLE 3 Number Average Molecular Weights of Poly-MHS Prepared in Different Phases

Temp. of Preparation °C	Phase	MW
115	Mesomorphic	17,500
115	Mesomorphic (magnetic field)	14,000
127	Isotropic	16,000

Experiments conducted in a magnetic field of 1300 Oe, which should be sufficient to affect the degree of order in a bulk sample of an anil type liquid crystal,⁽¹⁴⁾ also showed no effect on either the rates of polymerization or the nature of the polymer obtained.

Our results are not in accord with those of Amerik and Krentsel⁽⁸⁾ and Amerik *et al.*⁽⁹⁾ for polymerizations performed in either a smectic phase or for a solute monomer in a smectic solvent, but, as already indicated, there is dispute about the properties and hence the purity of the vinyl oleate employed. A similar controversy exists when considering certain low temperature free radical polymerizations where Adirovich⁽¹⁵⁾ and Semenov⁽¹⁶⁾ have postulated the existence of ordered monomer domains in liquid phases at low temperature. North⁽¹⁷⁾ reinvestigated the case of the low temperature free radical polymerization of methyl methacrylate near the freezing point of the monomer and concluded that, if ordered domains do exist in the liquid, they do *not* affect the polymerization process (or the domains are unaffected by dilution).

In the case of the liquid crystal polymerization studied here, it is equally clear that little, if any, effect of phase on the nature of the reaction exists. It is most likely that the order that exists before the reaction begins is destroyed on a microscopic scale as the reaction goes on, and that the thermal barrier to reaction is therefore the dominant and unchanged process as one moves from semi-ordered to isotropic phase.

Another factor which may affect the order of the matrix is mechanical agitation caused as the catalyst decomposes. This effect is probably small and restricted to the early stages of the reaction, but it may complicate the analysis of the kinetics. The smectic phase is, undoubtedly, a more rigid phase where topochemical effects might be more likely. The smectic monomers prepared in this study do polymerize in both the liquid crystalline and isotropic phases, but thus far the compounds have not been obtained in a sufficiently pure state to warrant a detailed kinetic study. The conclusion we are left with is that it appears unlikely that nematic phases are supportive of topochemical reactions.

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