Binary Mixtures of Liquid Crystalline Ester Bismaleimides

Andrea E. Hoyt[ab]; Samuel J. Huang[a]

[a] Polymer Science Program University of Connecticut, Storrs, Connecticut [b] Microsensors R&D, MS0351, Sandia National Laboratories, Albuquerque, NM

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BINARY MIXTURES OF LIQUID CRYSTALLINE ESTER BISMALEIMIDES

ANDREA E. HOYT† and SAMUEL J. HUANG*

Polymer Science Program
University of Connecticut
Storrs, Connecticut 06269-3136

ABSTRACT

A binary system consisting of a chlorohydroquinone-based ester bismaleimide (3-Cl), T_m = 238°C, and a methylhydroquinone-based ester bismaleimide (3-Me), T_m = 251°C, was investigated for the purpose of improving processability by widening the nematic phase range before polymerization. Calculations based on the Schroeder–van Laar equation predicted a system eutectic composition of 41% 3-Me monomer and a eutectic temperature of 202°C. Experiments found the eutectic composition at 35% 3-Me and the eutectic temperature at 218.5°C. Discrepancies between experimental results and theoretical predictions are likely due to error in measured heats of fusion either due to impurities in the samples or due to the reactive nature of the components being considered. Thermal cycling was also found to have a significant melting point depression effect. While significant depression of the system melting point was achieved, polymerization still occurred immediately after melting in all systems evaluated. All mixtures could be polymerized from the nematic phase to yield a solid which retained the nematic orientation of the starting polymer melt.

†Current address: Microsensors R&D, MS0351, Sandia National Laboratories, Albuquerque, NM 87185-0351.

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INTRODUCTION

Recently, there has been great interest in the synthesis, properties, and applications of liquid crystalline polymers (LCPs). The primary reason for increasing interest in LCPs is the enhancement of physical and mechanical properties that are introduced by the ordering of chains in these materials. However, one of the problems with conventional LCPs, particularly nematic LCPs, is that the enhancement of physical properties is unidirectional. The interactions between aligned chains are limited, van der Waals interactions and hydrogen bonding between amide chains being examples of such interchain interactions. These relatively weak interactions are not sufficient to prevent the polymer chains from pulling apart, thus producing a weakness in the direction perpendicular to chain alignment. Thus, improvement in the transverse properties of LCPs is desirable. One way to introduce three-dimensional strength would be through forming networks in liquid crystalline systems. Many researchers in the United States and abroad are pursuing liquid crystalline networks for various reasons. Major goals include the improvement of coatings, fibers, molded articles, and matrices for high performance fiber reinforced composites as well as applications in nonlinear optical materials. Several different types of liquid crystalline networks, some elastomeric [1-8] and some rigid [9-14], have been synthesized, and theories have been developed [15-19] to predict the behavior of these networks.

In this work, a thermotropic (melt-processable) system based on ester bismaleimides was considered. Such a system might find applications in molded LCP articles or extruded fibers as an agent to improve properties transverse to the orientation direction or as high temperature adhesives, where low melt viscosities, low thermal expansion coefficients, and high temperature stabilities are desirable. While there are many potential applications for thermotropic ester bismaleimides, their use is severely limited because thermally induced crosslinking occurs virtually simultaneously with the melting of the materials in question. Polymerization occurs extremely rapidly once the monomer has melted, and thus any desired processing operation would have to occur very rapidly, much more rapidly than is practical. Consequently, it is desirable to widen the processing window for these bismaleimides by lowering the system's melting temperature. To some extent, this can be done by adding lateral substituents onto the main rodlike unit of the monomer. Such practice is well-known in the preparation of LCPs [20]. However, there is a limit to how large a substituent can be placed onto a short rod molecule before its anisotropic behavior is destroyed. Thus, the approach chosen here for lowering melting temperatures was a binary mixtures approach.

During the 1970s and early 1980s a significant amount of work was reported on mixtures of low molecular weight liquid crystals. These systems covered a wide range of applications such as temperature indicators [21, 22], electro-optic display devices [23], and use as solvents for nuclear magnetic resonance spectroscopy [24]. During the course of these investigations, a very large number of mixtures were investigated and a tabulation of those systems was published [25]. The solid–meso-phase transition temperatures for many systems were accurately predicted using a variety of methods. The Schroeder–van Laar equation has been found to be accurate for several systems [26-28]. An alternative prediction method based on iterations has also been used [29] and is particularly convenient for mixtures of *more*

than two components. Other calculations for solid–mesophase transitions and for mesophase–mesophase or mesophase–isotropic transitions have also been performed with varying degrees of success [30, 31].

Since 1981, very little work has been reported on eutectics in liquid crystalline systems, and no one has extensively investigated binary mixtures of highly reactive liquid crystals although such a system has been reported [14]. If the Schroeder–van Laar equation is applied to a system of reactive liquid crystalline monomers, a substantial reduction in the melting temperature relative to the pure monomers is predicted as in the case of the low molecular weight liquid crystalline materials investigated in the 1970s and early 1980s. It is this melting point depression which we wish to apply in an attempt to improve the processability of thermotropic liquid crystalline thermosets.

The materials utilized in this study were ester bismaleimides, based on methyl- and chlorohydroquinones, and N-(p-carboxyphenyl)maleimide, previously reported by Hoyt and Benicewicz [32]. The behavior of the two monomers, theoretical predictions, and experimental agreement with theory will be discussed.

EXPERIMENTAL

Sample Preparation

Bismaleimide monomers based on methylhydroquinone and chlorohydroquinone can be prepared as described in the literature [32]. The monomers used in this study were supplied by Los Alamos National Laboratory. Monomers were purified by recrystallization from either methylene chloride or chloroform. Chemical structures were verified using ^{1}H nuclear magnetic resonance spectroscopy (NMR), and purity was evaluated using elemental analysis.

Mixtures of bismaleimides were prepared by dissolving the two monomers in methylene chloride and then evaporating the solvent.

Characterization

Differential scanning calorimetry (DSC) was performed using either a DuPont DSC910 or a Perkin-Elmer DSC-7 differential scanning calorimeter. Samples were analyzed under a nitrogen atmosphere at a heating rate of 20°C/min and were quenched between successive scans. A quench rate of 100°C/min was employed when controlled cooling was available. Data are presented for heating cycles only.

Infrared spectra were collected using a Mattson Cygnus 100 Fourier Transform Infrared Spectrometer at a resolution of 4 cm^{-1}. Samples were deposited onto KBr windows and placed into a heating cell which was then placed in the spectrometer and heated to a temperature within the cure region as determined by DSC. Several scans were taken over a period of time at this temperature.

Polarized light microscopy was performed using a Nikon Labophot microscope equipped with crossed polarizers, a Kofler hot stage, and a camera assembly. Magnifications of 200× and 400× were used.

RESULTS AND DISCUSSION

Behavior of the Monomers

In order to understand the thermal behavior of the mixtures, it is important to first understand the thermal behavior of the monomers, whose chemical structures are shown in Fig. 1. The thermal behavior of the two monomers was investigated using differential scanning calorimetry (DSC) and hot-stage polarized light optical microscopy. Representative DSC thermograms for both monomers are shown in Fig. 2.

The behavior of the methylhydroquinone-based monomer, hereafter referred to as 3-Me, was very straightforward. The DSC curves showed a single endothermic transition corresponding to a crystalline to nematic transition which was also observed by polarized light microscopy. This sharp endotherm was followed immediately by an exothermic transition that was attributed to thermally induced polymerization of the maleimide endgroups. No nematic to isotropic transition was observed before crosslinking occurred, and the nematic texture observed in the melt was retained after crosslinking had taken place.

In contrast, the behavior of the chlorohydroquinone-based monomer (3-Cl) was very complex. The DSC curve exhibited either two or three endothermic transitions in addition to the exothermic transition which was again attributed to thermally induced polymerization of the maleimide endgroups. The number of endothermic transitions and the associated ΔH values observed were dependent on the previous history of the sample. The recrystallization solvent in particular had a major effect on the thermal behavior of the monomer. When methylene chloride was used, three endothermic transitions resulted, whereas the use of chloroform in recrystallization yielded two endothermic transitions.
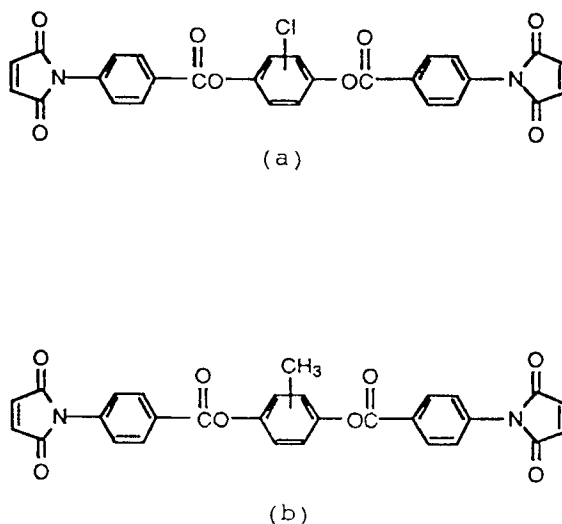
(a)

(b)

FIG. 1.   Structures of ester bismaleimide monomers: (a) 3-Cl monomer, (b) 3-Me monomer.
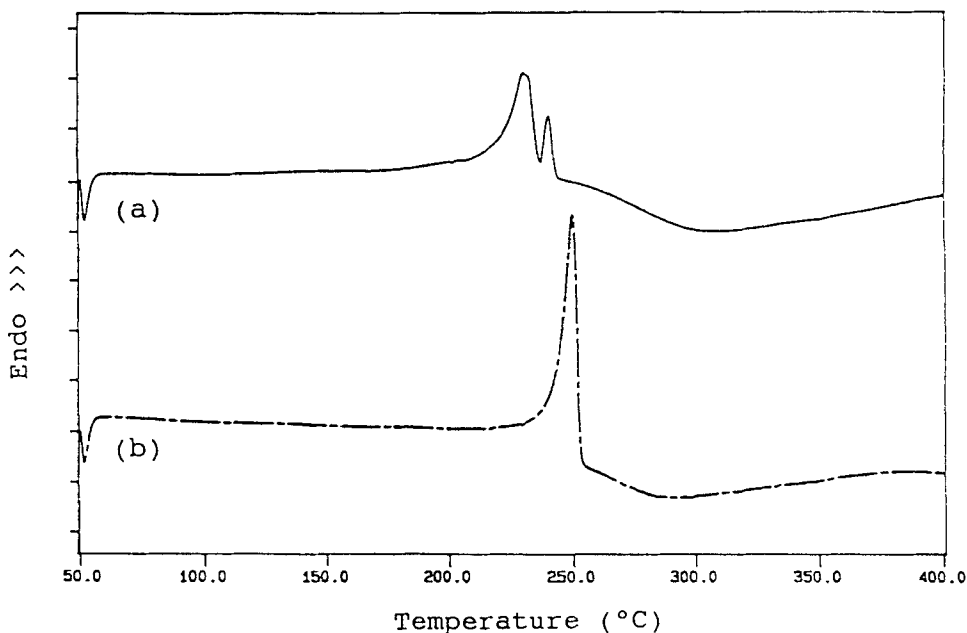
FIG. 2.   DSC thermograms of ester bismaleimide monomers: (a) 3-Cl monomer, (b) 3-Me monomer.

The nature of each endothermic transition was investigated before moving on to the analysis of the mixtures. The effect of heating rate on the endothermic transitions was also investigated. To first determine the nature of each endotherm, samples recrystallized from methylene chloride (thus exhibiting three endotherms) were analyzed at 20°C/min after being subjected to thermal pretreatments which were designed to simplify the thermograms. These pretreatments are described in the following paragraphs. Initially, the sample was heated to a temperature slightly above the peak temperature of the first transition and then quenched. No weight loss was observed, indicating no loss of volatiles from the sample. Upon reheating, only two endothermic transitions remained and the heat of fusion (ΔH_f) for the second transition had been increased. However, when the sample was observed using hot-stage optical microscopy, no melting was observed, leading to the conclusion that the lowest temperature transition of the original three endothermic transitions was a solid-state transition.

The second endothermic transition was investigated in the same manner. Again, no weight loss was observed and upon reheating of the sample, only one endotherm remained. The heat of fusion was increased by an amount which was slightly smaller than that of the now absent endotherm. However, in this case, hot-stage polarized light microscopy indicated some melting of the sample at a temperature corresponding to the second endotherm. It is important to note that the sample only showed partial melting at this stage. If the sample was heated past the final endothermic transition, a free-flowing nematic phase was observed before polymerization, after which the nematic texture was retained. As in the case of the

3-Me monomer, no nematic to isotropic transition was observed before crosslinking occurred in the sample. The onset temperature of polymerization remained the same regardless of the thermal pretreatment.

The multiple endotherm behavior of the 3-Cl monomer may be heating-rate dependent, that is, at slower heating rates the transitions may be forced to the more stable (higher melting) crystalline form. Consequently, the behavior of the 3-Cl monomer was investigated at several different heating rates: 40°C/min, 20°C/min, 10°C/min and 5°C/min. The results of these experiments are expressed in Table 1.

The total heat of fusion remained constant within experimental error regardless of the heating rate employed. The magnitude of ΔH_f associated with the highest temperature endothermic transition was larger when slower heating rates were employed. Previous research has indicated that metastable solid forms convert to the more stable solid form during standing for prolonged periods at room temperature [22, 29]. It was also stated that metastable crystals in mixtures could be removed by annealing [29]. A slow heating rate would allow for some of this annealing to take place during the course of a heating scan. However, any "annealing" that might have occurred was not complete and thus multiple endothermic transitions were observed over the range of heating rates investigated. It can be concluded that the 3-Cl monomer has at least one metastable solid form. In performing calculations to predict the phase behavior of a binary mixture containing this monomer, it was assumed that the total ΔH_f value (the sum of ΔH_f values for all endothermic transitions) could be used. The T_m used in the calculations was that for the most stable (i.e., highest melting) crystals.

The Calculated Phase Diagram

In the next stage of the work, binary mixtures of the two monomers discussed above, 3-Cl and 3-Me, were considered. A phase diagram for a binary system of liquid crystalline materials can be calculated using the Schroeder-van Laar Equation [26–28]

$$-\ln \phi = \frac{\Delta H_f}{R}\left(\frac{1}{T} - \frac{1}{T_m}\right)$$

where R is the gas constant, ϕ is the mole fraction of monomer in the mixture, ΔH_f is the heat of fusion of the monomer, T_m is the melting point of the pure monomer, and T is the melting point of the mixture. The equation is solved for T at several

TABLE 1.   Effect of Heating Rate on 3-Cl Monomer Transitions

Heating rate, °C/min	Transition temperatures, °C		Total heat of fusion (ΔH_f), J/g
40	Shoulder ~237	237	57.52
20	233	241	57.85
10	230	240	55.18
5	229	239	59.00

TABLE 2.   Thermal Data Used in Phase Diagram Calculation

Monomer	Heat of fusion (ΔH_f), J/g[a]	Transition temperature (T_m), °C[a]
3-Cl	54.68 ± 1.41	237.6 ± 0.7
3-Me	71.48 ± 2.89	250.8 ± 1.0

[a]Error reported as standard deviation from the mean.

values of ϕ for each component. The values employed for ΔH_f and T_m were determined experimentally and can be found in Table 2.

The results were plotted as shown in Fig. 3. The eutectic point was considered to be the intersection of the two curves. The composition could be calculated by solving simultaneous equations assuming a single value for T or alternatively by using the iteration method of Hulme, Raynes, and Harrison [29]. The eutectic composition for this system, calculated using the method of Hulme et al., is at a mole fraction of 3-Me $\phi_e = 0.41$. The theoretical eutectic temperature, $T_e = 202$°C, was also calculated. Clearly, if the theory is correct, the goal of lowering melting temperatures, thereby increasing system processability, is accessible.

Experimental Results and Discussion

When investigating the mixtures, some samples exhibited multiple endothermic transitions similar to those observed for the 3-Cl monomer. An obvious conjecture is that the mixtures exhibit polymorphism as observed for the 3-Cl monomer. Indeed, polymorphism is well known in mixtures, particularly if one of the compo-
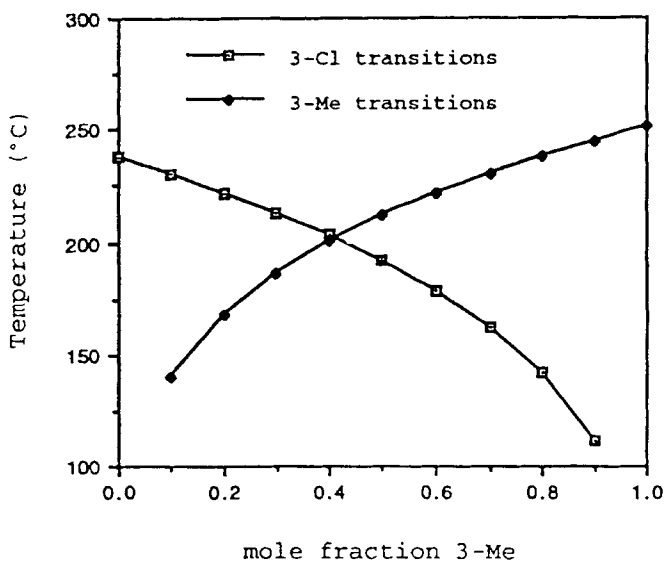

FIG. 3.   Calculated phase diagram for 3-Cl/3-Me mixtures.

nents is known to exist in metastable forms [33]. Therefore, in order to simplify the thermal behavior somewhat, the samples were subjected to a pretreatment. If the samples are pretreated by heating to ~200°C followed by quenching, any endothermic events corresponding to the solid-state transition in the 3-Cl monomer should be removed. Indeed, no transitions were observed ~180°C when the samples were reheated. However, for some samples there were still two melting endotherms. Consequently, a slightly different pretreatment procedure was investigated. For this procedure the sample was quickly heated past all melting endotherms, to ~245°C, and then quenched in an attempt to prevent polymerization of the sample. Reheating of the quenched samples yielded thermograms exhibiting a single crystallization exotherm followed by a single melting endotherm and the polymerization exotherm. In all cases the onset temperature of polymerization was unaffected by the pretreatment.

The plot of melting temperatures vs mixture composition, $\phi_{3\text{-Me}}$ is shown in Fig. 4. An interesting feature became noticeable when the melting temperatures of the mixtures were compared for samples with identical composition, but with different pretreatments. For any composition $\phi_{3\text{-Me}}$, the melting temperature of a sample experiencing the 200°C pretreatment was higher than that for the same mixture receiving the ~245°C pretreatment. Additionally, a double eutectic appeared in the phase diagram over the composition range $\phi_{3\text{-Me}} = 0.25$ to $\phi_{3\text{-Me}} = 0.5$ after the first heating cycle. These two phenomena were explored independently.

Hoyt and Benicewicz reported a depression of melting temperature during the course of thermal cycling for methylnadimide endcapped esters of similar structure to the bismaleimides investigated here [32]. It was speculated that this melting point depression was due to the formation of an extremely complex mixture of materials arising from the thermally induced polymerization of the original monomer mate-
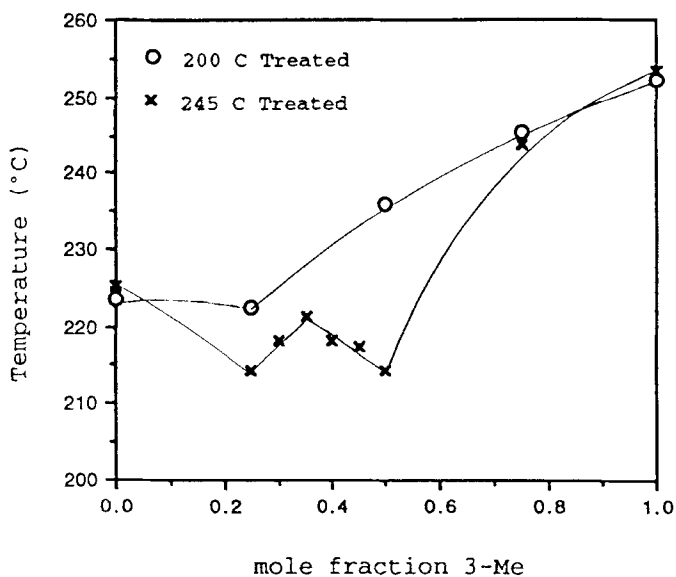

FIG. 4. Phase diagram for 3-Cl/3-Me mixtures, 200°C vs 245°C pretreatment.

rial. There is also a possibility that the melting points could be observed at lower temperatures simply because the crystals that are available to melt are significantly smaller than those found in the original mixture. Similar behavior has been reported for various epoxy-terminated liquid crystals [34] and for some photocrosslinkable liquid crystalline acrylate systems [35], although possible reasons for the behavior were not discussed. It is believed that at least some of the melting point depression observed for the bismaleimide mixtures receiving the higher temperature pretreatment may be in part due to the reasons discussed by Hoyt and Benicewicz. Thermal cycling experiments were undertaken in an effort to determine if further lowering of the melting temperatures could be achieved. This, in fact, was the case as shown by the plot in Fig. 5. Over several heating cycles at 20°C/min, melting temperatures were depressed by a significant amount relative to the original melting points of the mixtures. However, as thermal cycling proceeded, any melting endotherms observed showed successively lower values for the heat of fusion. This is due to the fact that some polymerization occurred during each heating cycle. Eventually, the sample was almost completely polymerized and melting was no longer observed.

Similar behavior was observed when the thermal cycling experiments were performed at 5°C/min. The fraction change in the melting point over the course of one heating cycle is larger at a heating rate of 5°C/min than at 20°C/min. This could possibly support both conjectures regarding the reasons for melting point depression during thermal cycling. More reaction of the monomers would be expected to occur at a slower heating rate, thus yielding a more complex mixture in one cycle than would be attained at a faster heating rate. Alternatively, as a consequence of more reaction occurring during the slower heating cycle, there would be less material available to crystallize into smaller crystals, thus lowering the melting point. In actuality, the observed melting point depression as a result of thermal
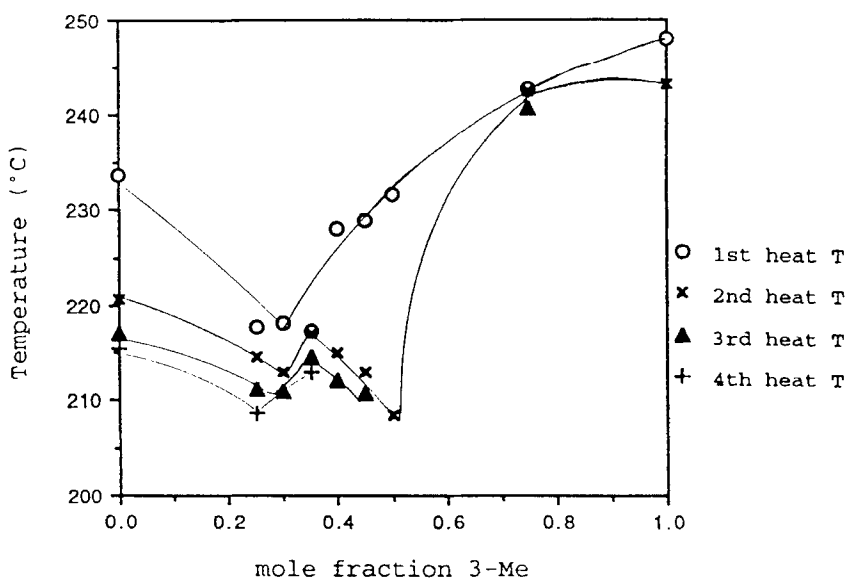

FIG. 5.   Phase diagram for 3-Cl/3-Me mixtures, effect of thermal cycling.

cycling is probably a combination of the two effects, and at this time the major contributor to the melting point depression cannot be determined.

In addition to the melting point depression occurring during thermal cycling, double eutectic behavior became noticeable. In the first heating scan, the double eutectic was not observed although there did appear to be a range of approximately equal melting temperature. However, such behavior has been previously reported for nematic mixtures used as solvents for NMR [24] and will not be discussed here. In subsequent heating cycles, the double eutectic became extremely pronounced. When dealing with reactive components, compound formation is possible. If such a compound is formed, the phase diagram would be expected to show a eutectic composition between each of the pure components and the compound formed from the two. This would result in the type of double eutectic observed for the 3-Cl/3-Me system. Compound formation between 3-Cl and 3-Me is logical when the reactive maleimide endgroups and facile crosslinking during heating are recalled. However, compound formation must be confirmed, and to do this, Fourier transform infrared spectroscopy was employed.

A thin layer of the mixture powder was solvent-deposited onto a KBr window and then placed into a heating cell which was placed into the spectrometer. The sample was then heated to a temperature slightly above the melting temperature of the sample. Spectra were then collected every few minutes during a 30-minute time period. To look at the most likely reaction of the 3-Cl and 3-Me monomers, the polymerization of the maleimide double bond, the disappearance of the olefin $C-H$ stretch band at 3100 cm^{-1} was monitored. If quantitative results are desired, the methyl $C-H$ stretch band at 2960 cm^{-1} can be used as an internal standard. This will correct for any changes in sample thickness due to flowing of the sample. Over the time period tested, the olefin $C-H$ stretch band became smaller relative to the methyl $C-H$ stretch band. The peak area of the olefin $C-H$ stretch was ratioed to the peak area of the methyl $C-H$ stretch and plotted as a function of time. This plot is shown in Fig. 6. The peak area ratio became constant within 30 minutes and at longer times attained a constant nonzero value. The nonzero value is indicative of unreacted double bonds remaining in the sample. The presence of unreacted double bonds is most likely due to both lack of mobility and large distances between double bonds remaining in the system.

Optical Polarized Light Microscopy

All mixtures melted into a freely flowing nematic phase as observed by optical polarized light microscopy. For several of the mixtures there appeared to be two different melting points, corresponding to observed DSC endotherms. Both led to a nematic phase. Optical observation indicated that some of the samples began to clear to isotropic shortly after melting into a nematic comesophase and shortly before significant polymerization occurred. Upon polymerization, the texture generally remained nematic, although in some cases some isotropic areas were observed after crosslinking. No nematic to isotropic transitions were observed in the DSC thermograms. However, it is likely that such transitions would be obscured by the large polymerization exotherm which immediately follows the highest temperature melting endotherm for all samples. In discussing the curing of liquid crystalline bisnadimide monomers, Hoyt and Benicewicz indicated that the ultimate product of
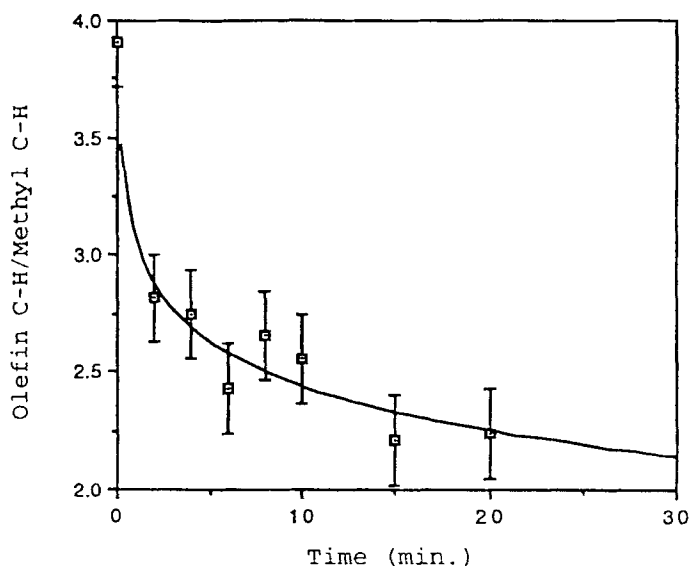
FIG. 6. Peak area ratio (olefin C—H/methyl C—H) vs time.

polymerization should be a nematic solid [32]. This is regardless of whether or not a nematic to isotropic transition can be observed. Such behavior has been observed experimentally [34, 36]. Similar behavior should be expected for the mixtures of bismaleimides. Several of the mixtures showed transitions to an isotropic phase, but the polymerized samples exhibited a predominantly nematic texture although some isotropic areas remained. It is possible that unoriented and unpolymerized materials (isotropic) material could have been trapped in the system as polymerization occurred and the glass transition temperature rose above the temperature used for the investigation, thus inhibiting the mobility and further polymerization in the system. The presence of isotropic and biphase polymerized material such as that observed here has also been observed by Benicewicz and colleagues for bisacetylene ester monomers [37]. A polarized light photomicrograph of a polymerized mixture is shown in Fig. 7. The schlieren texture typical of a nematic phase is clearly observed.

Comparison of Theory and Experiment

In order to compare the prediction of eutectic composition and temperature with the experimental results, only the first heating cycle can be considered due to the complexities (melting point depression and double eutectic behavior) which developed during subsequent heating cycles. Experimentally, the observed eutectic composition was found at $\phi_{3-Me} = 0.35$ regardless of the heating rate employed. The eutectic temperature was only slightly dependent upon the heating rate, found at 219.9°C for a heating rate of 5°C/min and at 217.1°C for heating rate of 20°C/min. The predicted values for the eutectic composition and the eutectic temperature were $\phi_e = 0.40$ and $T_e = 201$°C. For the system under consideration, the agreement between predicted values and experimental data was not very good, in contrast

FIG. 7.   Polarized light micrograph of a polymerized LCT mixture.

to previous work done with nonreactive liquid crystals in which the correlation of theory and experiment was excellent [26–28].

It has been demonstrated that deviations from ideal behavior, which may occur as a consequence of specific intermolecular interactions or structural similarity, can have a significant effect on the phase behavior [8, 12]. However, in this case the major contributor to the disagreement is probably the presence of impurities in the samples. The impurities can be of any nature, including residual solvent or unreacted starting materials. Ideally, in order to obtain materials of suitable purity for thermodynamic measurements, the chosen purification methods would not involve any solvent, as in sublimation or zone refining. However, for the reactive system considered in this work, these methods would involve heating to a temperature which might be high enough to induce polymerization. Thus, purification is limited to solvent-based techniques such as recrystallization. In the case of the 3-Cl monomer, impurities in the bismaleimide could also arise from impurities present in the reagents used in monomer synthesis. Gas chromatography/mass spectrometry indicated that small amounts of unsubstituted hydroquinone and dichlorohydroquinone were present in the chlorohydroquinone starting material. If the amounts of these impurities were small and approximately equal, they might not be detected with the techniques employed here. Although purity of the monomers was assessed using nuclear magnetic resonance spectroscopy and elemental analysis, it is possible that small amounts of trapped recrystallization solvent or impurities arising from the starting materials used in monomer synthesis were still present in the sample. Impurities present at concentrations as low as 0.01 mol%, well below the detection

limit of NMR, can have a significant effect on heats of fusion and temperatures of transitions [38]. Such impurities could result in low values for the heats of fusion and transition temperatures of the two monomers. Since these experimental values were used in the calculations of the eutectic composition and eutectic temperature of the system, a discrepancy between calculations and experimental data might be expected. Other complications, such as polymorphism in the 3-Cl monomer and the reactive nature of the two materials, may also play a significant role in the discrepancies observed between theoretical prediction and experimental data.

CONCLUSIONS

The binary mixtures approach was successful in lowering the system transition temperature relative to both the 3-Cl monomer and the 3-Me monomer. The eutectic temperature measured during the first heating cycle was at an average temperature of 218.5°C, which is 19.1°C below the melting temperature of the most stable 3-Cl crystals and 32.4°C below the melting temperature of the 3-Me monomer. However, an improvement in processability was somewhat debatable as thermally induced polymerization still began as soon as the material had melted.

Thermal cycling of the mixtures indicated a substantial decrease in the melting temperature of the remaining crystals in the subsequent heating cycle. The heat of fusion observed also decreased with successive heating cycles. The exact reasons for these two phenomena are not known, although formation of extremely complex mixtures and formation of smaller monomer crystals are expected to be contributors.

ACKNOWLEDGMENTS

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