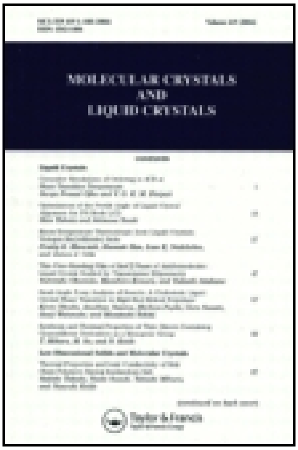

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Kinetic Feature of Nematic Phase Polymerization of Diacetylenes

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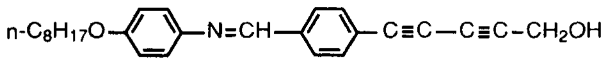
Nematic phase polymerization of diacetylenes proceeded without an induction period. The decay rate of monomers was found to be enhanced in a thin film sample. When an external electric field was applied to the thin film, the rate was accelerated with a threshold value of 2500 V/cm which corresponds to that for a dynamic scattering mode.

Keywords: diacetylene, nematic phase polymerization, polydiacetylene

INTRODUCTION

Solid state polymerization of diacetylenes[1] has drawn attention not only from the potential utility of a highly conjugated π system in the resulting polydiacetylenes[2] but also from the mechanism of formation of polymers in organized media.[3] In order to examine the effect of the reaction media on the kinetic behavior of diacetylenes in detail it may be extremely interesting to study the reactivity of mesogenic diacetylenes not only in a crystal phase but also in liquid crystal ones.[4] Although there are some scattered examples of nematic phase polymerization of diacetylenes,[5] its kinetic feature has not been explored yet. Here we report some characteristics in the nematic phase polymerization of mesogenic diacetylene (1) especially in a thin film under an external electric field.



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EXPERIMENTAL

Diacetylene monomer 1 with a mesogenic core of benzylidene(4-octyloxy)aniline moiety was prepared by the condensation of 4-octyloxyaniline (2) and 4-(5′-hydroxy-1′,3′-pentadiynyl)benzaldehyde[6] (3). Monomer 1 was confirmed to have a nematic phase above 123°C from observation of schlieren texture under a microscope. The dynamic scattering mode (DSM) was observed when electric fields larger than 2500 V/cm was applied. (The observation of DSM is consistent with the dielectric anisotropy of 1, its perpendicular component being larger than the transverse[7]). The decay of the monomer was monitored by the decrease in the absorption intensity of $\nu_{C\equiv C}$ band (2235 cm^{-1}). Film samples were heated in a sandwich-type cell.

RESULTS AND DISCUSSION

The decay curve of 1 in the nematic phase at 130°C shows a smooth exponential trace with little induction period (Figure 1), showing a sharp contrast with the reactivity in the solid state polymerization of diacetylenes: e.g. 2,4-hexadiyne-1,6-diol bis(p-toluenesulfonate) (PTS) has a few hours of an induction period at 80°C.[3,8] As the products are accumulated in the reaction medium, the decay rate of the monomer decreases gradually. The above results may be rationalized in that local motions are not so restricted as in the solid state and that the neighboring monomers

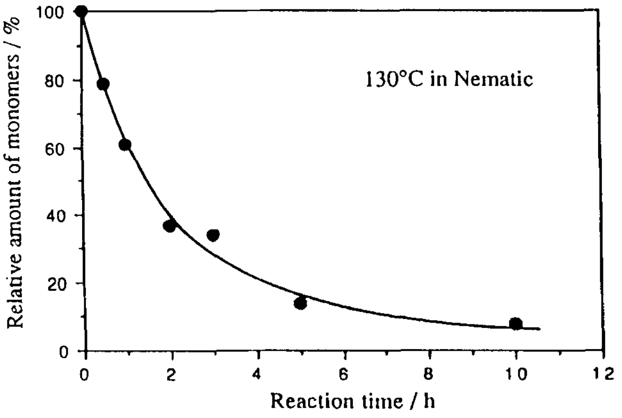

FIGURE 1 The decay curve of the monomer 1 at 130°C.

in the nematic phase have a chance to align to the favorable orientation for 1,4-addition by thermal fluctuations. The flexibility of the nematic medium, however, decreases with increasing amount of products. After heating for 24 h, the obtained polymer was insoluble to any organic solvent. There are no signals assignable to acetylenic carbons, which are observed in the monomer, in a high resolution solid state ^{13}C NMR (CP/MAS) spectrum.[9] An absorption spectrum of the polymer extends over to 700 nm. These spectroscopic data are consistent with the structure of polydiacetylene formed by 1,4-addition.

Besides the inductionless decay of 1, the nematic phase polymerization was found to have the following kinetic features which are characteristic to the mesogenic reaction medium. First, the initial rate of polymerization of 1 was enhanced when a sample was placed between parallel glass plates. The conversion of 1 in a thin film sample was measured after 3 minutes at 123°C by changing the thickness of the sample (Figure 2). The decay rate in the sample of 150 μm thickness is practically the same as that of the bulk. The enhancement in rate was obviously observed when the thickness becomes thinner than 100 μm. This result suggests that the reactivity of the monomer becomes higher as the order in orientation of monomers increases in thinner films.[10]

Second, the polymerization rate was found to be accelerated by applying an external electric field to the sample in a thin film (50 μm). Field strength (E) dependence on the conversion of 1 at 123°C after 3 minutes is shown in Figure 3. The plot shows a presense of threshold value of 2500 V/cm for the rate acceleration, and it has a broad maximum at 8000 V/cm. The decay rate of monomer 1 increases by three times at this field strength compared with the initial value. The conversion of 1, however, decreases gradually at a higher electric field than 8000 V/cm. These results clearly show that the external electric field makes the monomer align[7,11] to the favorable local orientation for polymerization at higher field strengths than the threshold value, which corresponds to that for DSM in the present case. On the other hand, large structural fluctuations could also disturb the alignment of mono-

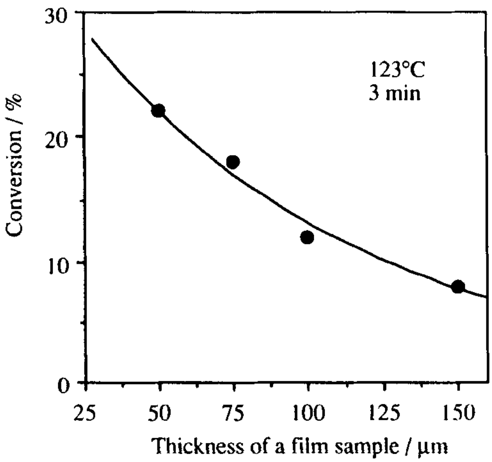

FIGURE 2 Thickness dependence of conversion of 1.

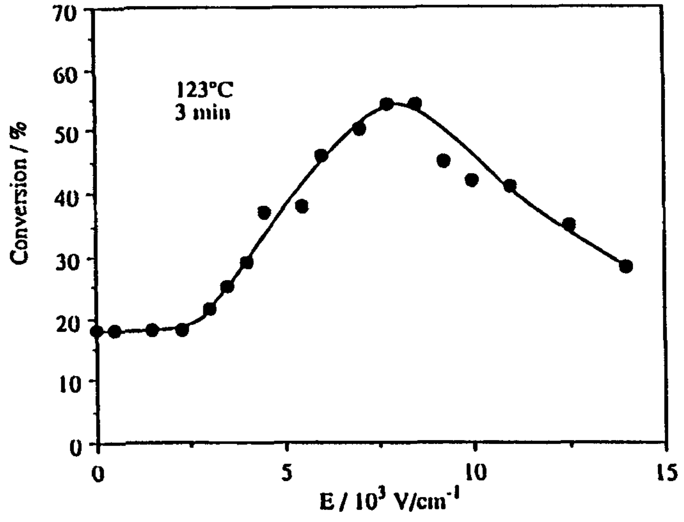

FIGURE 3 Field strength dependence of conversion of 1.

mers and prevent monomers from locating at the favorable orientation. These two competing factors result in a convex curve in the plot of the field dependence of the reaction rate.

CONCLUSION

In summary, we observed that the polymerization of 1 occurs smoothly without an induction period in the nematic phase. The nematic phase polymerization shows the thickness dependence of a film sample on the polymerization rates. The remarkable external electric field effect on the initial rate of polymerization is also observed. The thermal reactivity of diacetylene was found to largely reflect order and freedom of local motions of monomers in the nematic medium. These kinetic features may lead to a subtle control of the reactivity of diacetylenes in nematic media.

Acknowledgment

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