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Polymerization of bisacrylic monomers within a liquid-crystalline smectic B solvent

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A smectic B (S_B) solvent may provide a very highly ordered, and possibly oriented, host medium for polymerization processes. Photochemical polymerizations of two bisacrylic monomers were therefore carried out in a S_B medium. The process conditions were chosen on the basis of a preliminary study of the monomer-solvent binary system carried out by differential scanning calorimetry (D.S.C.), optical microscopy and X-ray diffraction. The polymerization was then studied by D.S.C. at different reaction times. These measurements showed clearly that there is a point along the reaction path at which the growing polymer chains start segregating from the solvent and the mesomorphic bulk no longer acts as a reaction solvent but only as a reservoir for the monomer. The polymer chains from that point keep growing only upon or between the faces of the S_B layers. Electron microscopy observations showed that the morphology of the final polymer is affected by this interlayer process.

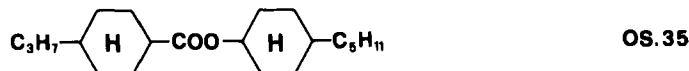
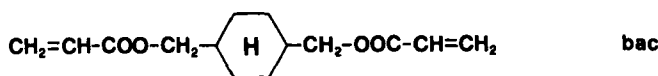
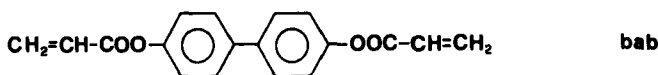
1. Introduction

When a non-mesomorphic solute is dissolved in a liquid crystal the correlations of the molecular orientations, and hence the ordering of the mesomorphic solvent, are locally disturbed. The tendency of the solvent to keep its lowest energy undisturbed state provides a driving force which gives rise to constraints to the conformations of the solute molecules and anisotropy in their orientation and translational diffusion [1]. If the molecular collisions inside the mesomorphic solution can promote a reaction of the solute molecules, the solvent ordering may drastically affect the stereochemistry and the rate of the process [2-4].

The synthesis of highly oriented polyacetylene within a nematic solvent has recently been reported [5]. But the local, short-range, orientational order of a nematic solvent is expected to be very similar to that of isotropic solvents [6]. The ability of a mesomorphic solvent to affect the course of a reaction ought to be linked to the rigidity of its molecular packing. Therefore highly ordered smectic mesophases could be much more effective to this end than nematic or cholesteric solvents. On this basis we have been searching for catalytic effects exerted by smectic solvents. We have found that S_B solvents are able to promote a reaction not attainable in other solvents [3]. Therefore the attempt to carry out photochemical polymerizations as well in the same S_B solvents was an attractive extension of this research into the polymer field.

2. Results and discussion

We chose a liquid crystal, recently marketed by E. Merck under the code OS-35, as mesomorphic solvent because it forms a smectic B phase at room temperature and it is transparent to near-U.V. and visible radiation [7]. It melts at 26°C and its clearing point is at 54°C. We chose 1,4-trans-bisacryloyl-cyclohexandimethanol (*bac*) as the monomer because its structure is closely similar to that of the solvent. Polymerizations of 4,4'-bisacryloyl-biphenyl (*bab*) were carried out in conjunction with it.



Reactivity investigations dealing with almost crystalline solvents must always rely on a detailed knowledge of the system within the reaction pot and therefore rely on the support of as many techniques as possible. At the very least, D.S.C. analysis, optical microscopy and X-ray diffraction measurements must be used to keep the structural modifications of the solute-solvent system during the reaction course under constant observation.

2.1. Thermal analysis and X-ray diffraction of the monomer-solvent mixture

The solubility of the guest monomer may be limited by the very high, almost crystalline order of the solvent. The solute-solvent, two-component system was therefore studied within the relative concentration range chosen for the polymerization reaction. The monomer was easily dissolved in OS-35 by heating the mixture to its nematic or isotropic phase.

D.S.C. thermograms of the mixtures at increasing concentration of *bac* are shown in figure 1. The first thermogram (*a*) is that of the pure solvent: it shows two peaks, labelled (1) and (2), from higher to lower temperatures, relative to the transition from isotropic (I) to nematic (N) and from N to S_B phases respectively. On increasing the *bac* concentration in the two-component system, the temperatures of the two transitions gradually lowered and their D.S.C. peaks broaden. This is due both to the gradual loss of cooperativity in the diffusion properties of the system and to the appearance of two-phase regions across the phase transitions [6].

In addition a new peak, labelled (3), starts to appear already at the very low *bac* concentration of thermogram (*b*), and its intensity increases with the *bac* concentration at the expense of the other two peaks. This new peak now dominates the whole thermogram (*e*), which corresponds to 0.19 M *bac* concentration. A very small shoulder (4) between peaks (2) and (3) is also indicated by thermograms (*c*) and (*d*). This very small signal which appears in a limited range of concentrations was confirmed by thermal analyses of OS-35 mixtures with other organic solutes [8]. The

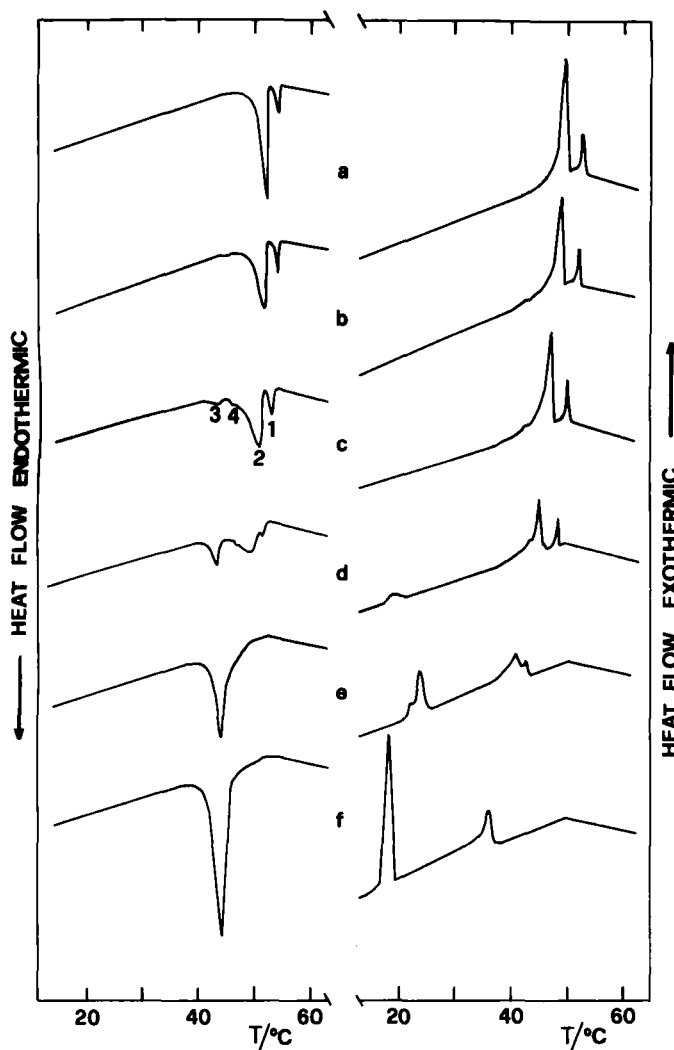


Figure 1. D.S.C. thermograms of *bac*-OS-35 mixtures where the monomer molar concentrations are (a) 0; (b) 1.77×10^{-2} ; (c) 3.83×10^{-2} ; (d) 7.36×10^{-2} ; (e) 19.04×10^{-2} ; (f) 29.7×10^{-2} . The left and right curves are measured in the process of heating and cooling, respectively.

temperatures of the maxima of peaks (1)–(4), obtained for the mixtures analysed, are reported in figure 2.

Optical microscopy showed that the solution is nematic between peaks (1) and (2), and smectic B after peak (2). The S_B mosaic texture remained unchanged when mixtures at low *bac* concentrations (lower than 5×10^{-2} M: region I of figure 2) were cooled down to room temperature. No isotropic phase through this smectic B region was revealed by either optical microscopy or linear dichroism studies [8] in very dilute OS-35 solutions. An unusual isotropic phase through the nematic or smectic phases, which may be a cubic or a plastic phase, was claimed very recently to be promoted by solutes [9]. The fraction of this new phase was seen to increase with the relative quantity of the guest molecules. Only by increasing the *bac* concentration (region II of figure 2) was a separation of an isotropic phase observed in correspondence of

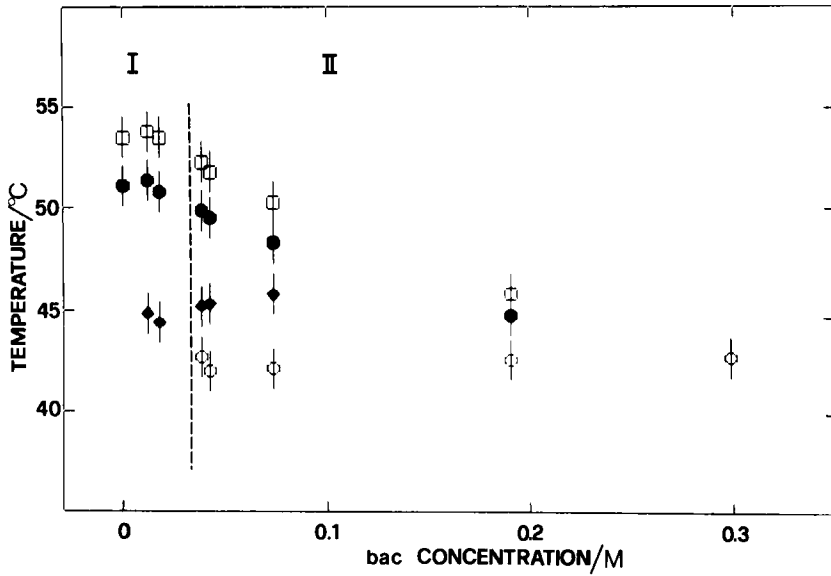


Figure 2. Temperatures of the transition peaks, labelled from (1) to (4), shown by the D.S.C. thermograms of two-component *bac*-OS-35 mixtures with monomer concentration up to 0.3 M.

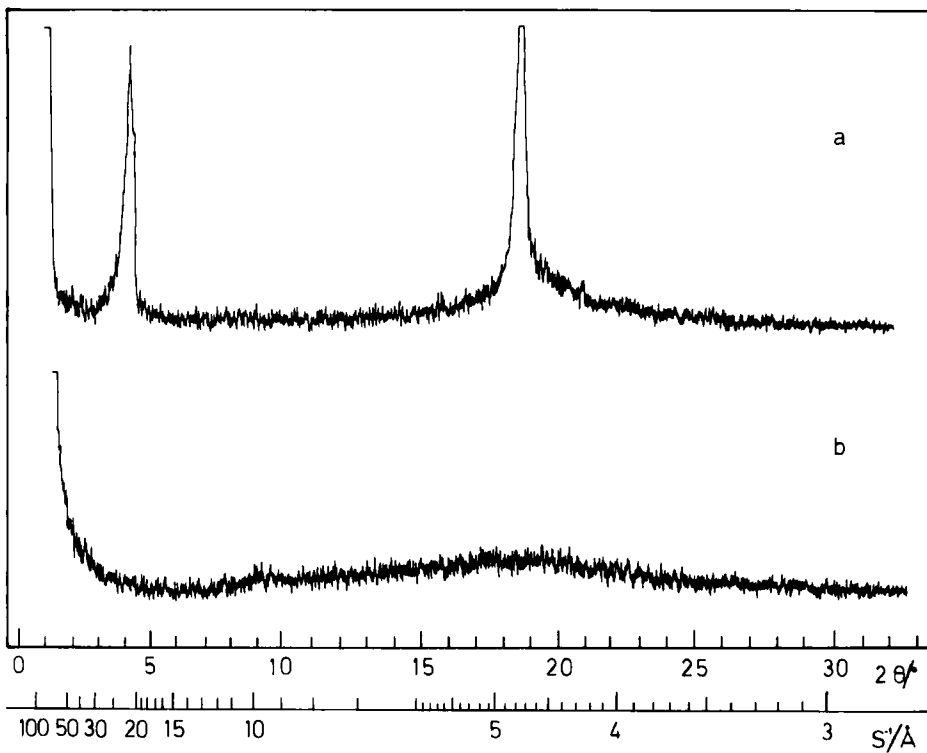


Figure 3. X-ray diffraction patterns of (a) OS-35-*bac* binary mixtures and (b) poly-*bac* synthesized in bulk or in the mesomorphic solvent.

D.S.C. peak (3). Our observations suggest the presence of a eutectic behaviour in OS-35 binary mixtures [8].

The X-ray scattering profiles showed by OS-35-*bac* mixtures are reported in figure 3. The interlayer and the intermolecular distances, which can be derived from the low- and high-angle peaks respectively, are not significantly affected by the presence of *bac*. The monomer molecules do not modify the overall long-range structural organization of the sample which determines the diffraction pattern [7]. This may be due to the fact that guest perturbations of a very highly ordered environment have a local, short-range effect only. It seems therefore that a very rigid three-dimensional array of host molecules may be unable to transfer the local guest perturbation to non-adjacent molecules as in the looser packing of a nematic phase. The pattern of the X-ray diffraction is also constant through all the smectic B region and no cubic or plastic phase was found by scanning at different temperatures. Therefore, on the basis of these D.S.C. and X-ray diffraction studies of the binary system OS-35-*bac*, we decided to carry out the polymerizations within region I of figure 2, i.e. at *bac* concentrations so low as to let the solvent smectic B thermogram be basically preserved.

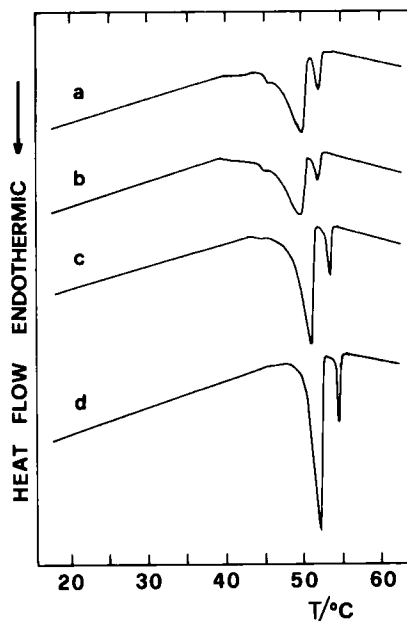


Figure 4. D.S.C. thermograms of the *bac*-OS-35 polymerization mixture at different reaction times: after (a) 0; (b) 25; (c) 95; (d) 195 min of irradiation.

2.2. Thermal analysis of the reaction mixture at different polymerization times

The reaction mixture was irradiated by an excimer laser (multilaser-306 nm). Figure 4 shows the D.S.C. thermograms at different reaction times. In the first 25 min, the oligomers increase in length and locally disturb the mesomorphic order of the solution more and more, with the solution transition temperatures gradually lowering and the peaks broadening. This trend, however, is suddenly reversed, i.e. the D.S.C. peaks start to become sharper and sharper, moving back toward higher temperatures. After 195 min, the D.S.C. profile becomes that of the pure OS-35 solvent, with no guest molecules being dissolved any longer. These D.S.C. measurements clearly

display that there is a point along the reaction course at which the growing polymers start segregating from the solvent, and the mesomorphic bulk no longer acts as a reaction solvent but only as a reservoir for the monomer. These reactant molecules may therefore diffuse towards the polymer which is forced to grow within the faces of the highly ordered S_B layers. This result basically confirms the conclusion of a study of Blumstein *et al.* suggesting that a linear polymer during its synthesis in a smectic solvent tends to be precipitated [10]. The phase of this solvent was afterwards shown to be a smectic C [11, 12].

It should be pointed out however that this segregation process was proposed on the basis of a binodal molecular weight distribution that now, in the light of more recent translational diffusion studies [1], may also match a polymerization process which is always in solution. In fact, the layered S_C structure may offer a guest molecule two different solubilization sites: within the rigid core layers and within the adjacent regions constituted by the flexible aliphatic tails. However, now the D.S.C. results shown in figure 4 offer clear-cut evidence that at least in our case the polymerization of a multifunctional monomer takes place mainly at the interface of the S_B layers. This may be reasonably assumed a general tendency for polymerizations in smectic solvents.

2.3. *Electron microscopy and X-ray diffraction of the polymer*

The polymer was isolated from the final reaction mixture by dissolving the liquid crystalline solvent in benzene.

X-ray diffraction studies of the resulting polymers gave no indication of induction of a smectic B pattern by the solvent. Figure 3 shows one of the resulting profiles obtained: they were all flat or very diffuse for polymers obtained in bulk or within the liquid-crystalline medium.

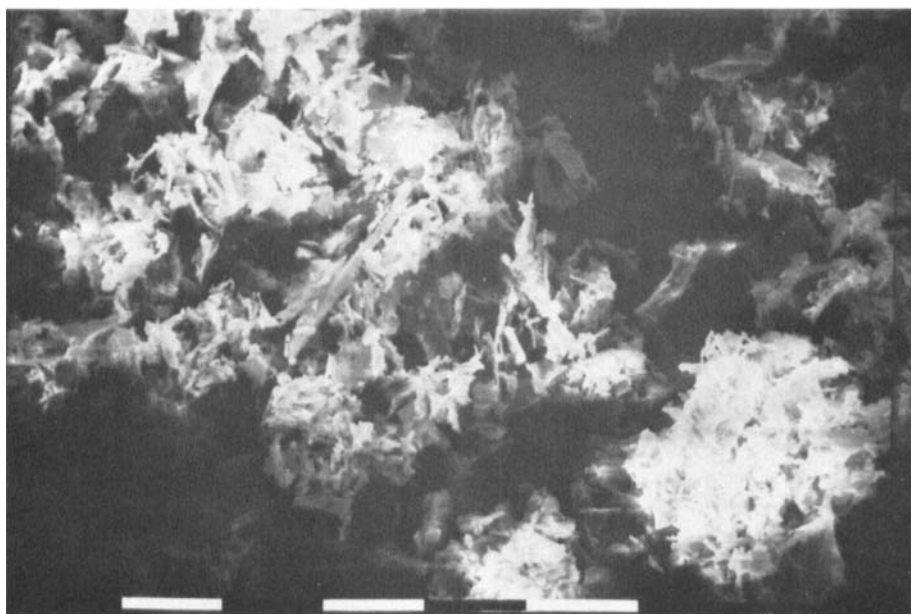
In contrast electron microscopy images (figures 5 and 6) of the polymer reveal differences between poly-*bac* synthesized in the S_B solvent or in the bulk. The inter-layer process, revealed by the D.S.C. analyses, seem to be in some way imprinted in the polymer morphology. In fact the sort of curled and indented flakes which appeared in its electron microscope images (cf. figure 5(a)) are also shown by the polymer of 4,4'-bisacryloyl-biphenyl, poly-*bab*, which was obtained by the same method (cf. figure 5(b)). These two polymers, poly-*bac* and poly-*bab*, are very different from each other in their morphologies when prepared in bulk (cf. figure 6).

The peculiar morphology shown by figure 5 is not determined by possible swelling processes during the extraction of the mesomorphic solvent by benzene. In fact figure 7 shows one electron microscope image of a poly-*bab* obtained in benzene solution: its morphology is totally different from that of the same polymer obtained in the smectic B solvent.

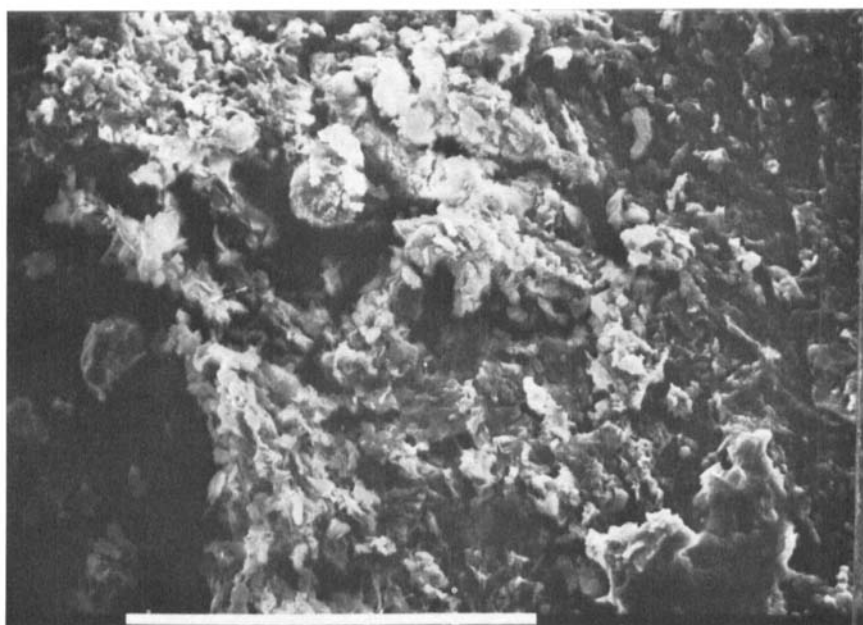
3. Conclusion

D.S.C. analysis of the *bac*- S_B solvent mixture at different reaction times clearly displayed that there is a point along the reaction course at which the growing polymer chains start segregating from, and are therefore forced to grow within or upon the faces of the highly ordered smectic B layers.

X-ray diffraction analyses of the resulting polymers did not reveal any induction of a smectic organization, and no differences between polymers obtained in bulk or in the mesomorphic solvent are shown by this technique. On the other hand electron



(a)



(b)

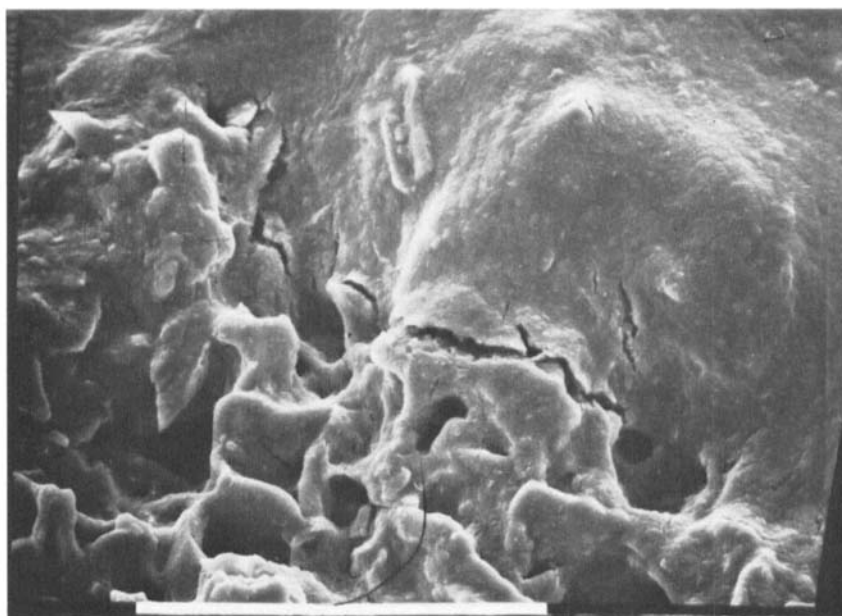
Figure 5. Electron microscope images of the poly-bac (a) and poly-bab (b) obtained within the smectic B phase of OS-35. The white bar corresponds to 0.1 μm .

microscopy observations showed that this interlayer process seems to be able to affect the morphology of the growing polymer.

A locally ordered polyacetylene has recently been prepared on the small-face surfaces of single biphenyl crystals [13]. It is precisely in the light of this result that the evidence reported in this paper of an interlayer polymerization process may draw



(a)



(b)

Figure 6. Electron microscope images of poly-*bac* (a) and poly-*bab* (b) prepared in bulk. The white bar corresponds to 0.1 mm.

further significance and prospects of possible developments. In fact they point the way to the use of a smectic B medium to provide almost crystalline [14], very wide surfaces which may be able to exert a driving force to the orientation of the growing polymer chains. It is well known that smectic B media may be homogeneously oriented into monodomain samples [15].

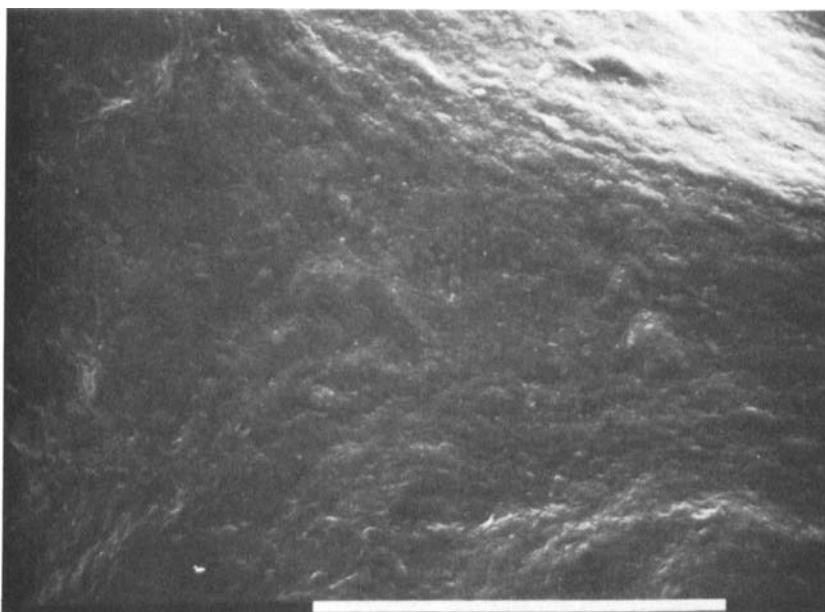


Figure 7. Electron microscope image of poly-*bab* prepared in benzene solution. The white bar corresponds to 0.1 mm.

4. Experimental

4.1. 4,4'-bis acryloyl biphenyl (*bab*) see [16]

1,4-*trans*-bis acryloylcyclohexandimethanol (*bac*) was synthesized by esterification of 1,4-*trans*-cyclohexandimethanol [17] with acryloyl chloride following the procedure of [16]. The reaction product was crystallized repeatedly from petroleum ether. Yield 70 per cent. m.p. = 81°C; ¹H N.M.R. (CDCl₃): (in p.p.m. from TMS) = 0.5–2.2 (*m*; 10H, aliphatic) 4.0 (*d*; 4H, OCH₂) 5.7–6.7 (*m*; 6H, vinyl).

The reaction mixtures were irradiated by an excimer laser (multilaser–306 nm) while following the reaction course by D.S.C. analyses. The polymer was then isolated by dissolving the liquid-crystalline solvent in benzene. The D.S.C. measurements were carried out on a Perkin–Elmer Calorimeter Model D.S.C.-2. The scan rate was 2.5°C/min. Aluminium containers of 20 μl capacity were used. The electron microscope images were obtained by a microscope Philips SEM 505 microscope at 15.1 kV.

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