Thermochimica Acta, 229 (1993) 299–310
Elsevier Science Publishers B.V., Amsterdam

Glass transition in semicrystalline systems [1]

U. Koy [a], H. Dehne [b], M. Gnoth [c] and C. Schick [a,*]

[a] *Department of Physics, University of Rostock, Universitätsplatz 3, D-18051 Rostock (Germany)*
[b] *Department of Chemistry, University of Rostock, Universitätsplatz 3, D-18051 Rostock (Germany)*
[c] *University of Ulm, Department of Applied Physics, Oberer Eselsberg, D-89081 Ulm (Germany)*

(Received 9 July 1993; accepted 19 July 1993)

Abstract

The investigation of amorphous layers between crystalline structures allows the estimation of glass transition length scales. Low molecular mass liquid crystals can form semicrystalline structures with amorphous regions smaller than 1 nm. In such structures we are able to investigate the breakdown of the co-operative molecular motions associated with the glass transition. The mixing of two liquid crystalline sulfur-bridged benzoates allowed the crystalline structure of the sample to vary. First calorimetric and dielectric investigations of different crystallized mixtures show significant differences in the relaxation behavior in the glass transition region.

INTRODUCTION

The glass transition is at present a central problem of condensed-matter physics [1, 2]. At the moment, there is no generally accepted theory of it. Therefore it is necessary to verify the theoretical approaches by independent experiments. One question is: What is the order of magnitude of the characteristic length of the underlying molecular processes? Previous experiments on semicrystalline polyethylene terephthalate (PETP) [3] show significant sensitivity of the glass transition parameters to the nanometer length scale. The results can be explained by a direct influence of spatial limitations on the large modes of the glass transition. We found that there is an actual correlation between the layer thickness of the amorphous region and the characteristic length of glass transition that we

---

* Corresponding author.

[1] Presented at the Tenth Ulm Conference, Ulm, Germany, 17–19 March 1993.

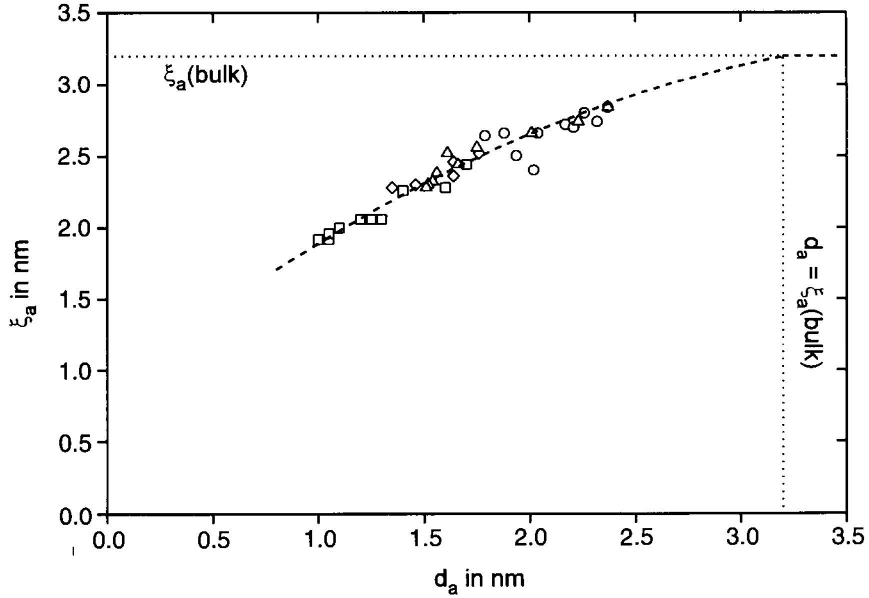

Fig. 1. Correlation length ξ_a (from thermal glass transition interval) as a function of amorphous layer thickness d_a (from SAXS, WAXS and Δc_p) for semicrystalline polyethylene terephthalate prepared by different crystallization regimes. The dotted curve is the extrapolation expected towards bulk amorphous sample [3].

get from Donth's fluctuation model [4]. Figure 1 shows the central result of our work on PETP [3].

The aim of this paper is to find a way to get more information about the glass transition in amorphous layers smaller than 1 nm: in this way we will try to observe the breadkdown of the co-operative glass transition process by extreme spatial limitations.

In previous work [4] it was shown that in special semicrystalline low molecular weight compounds an anomalous relaxation behavior in the glass transition region can be observed. In Fig. 2 [4] the relaxation processes of the 100% crystalline, the nematic and a semicrystalline sample of 3,3′-sulfonylbis[methyl 4-(4-*n*-pentyloxybenzoyloxy)benzoate] (Fig. 3) are presented. The very high value of the activation energy of process 4 (118 kJ mol^{-1}) suggests the idea that it could be a residuum of the glass transition due to strong spatial limitation. The anomalous behavior of the specific heat of the semicrystalline samples in the transformation interval (Fig. 4) supports this idea. Taking into account the temperature dependence of the characteristic length of the glass transition ($\xi_a \propto (T - T_\infty)^{-2/3}$ [5]) there should be a change from the Arrhenius like to WLF behavior at higher temperatures. Because of the decrease of ξ_a with increasing temperature there must be a temperature where the characteristic length becomes equal to the layer thickness and at higher temperatures no strong

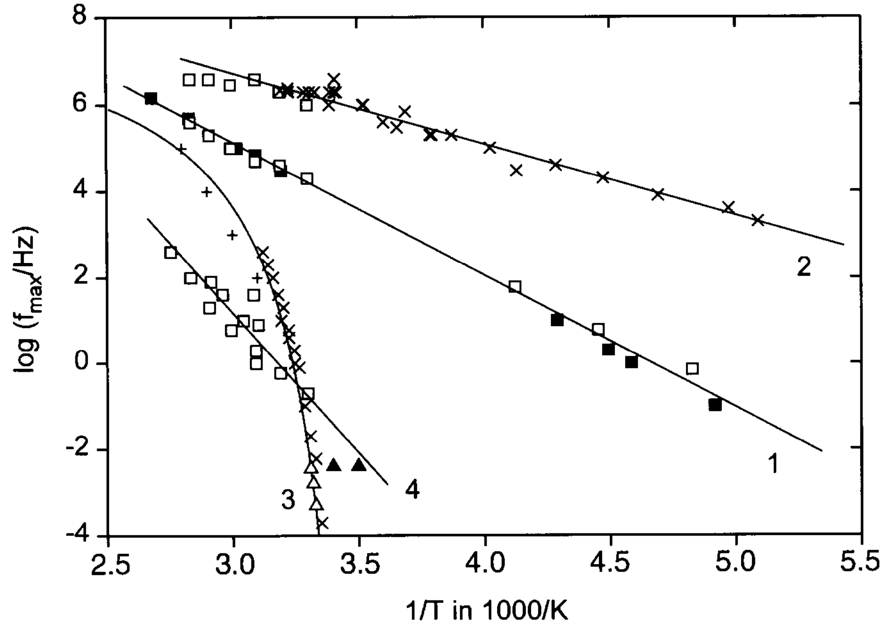

Fig. 2. Activation diagram of compound A from dielectric measurements [4]: f_m is the frequency of the maximum of tan δ. The 100% crystalline sample (■) shows only one local relaxation process (1). The nematic liquid (×, △) shows the typical behavior of a glass-forming substance — one local process (Arrhenius) (2) and a WLF-like glass process (3). For the semicrystalline sample (13 h at 310 K) (□) we can observe the two local processes (1, 2) but no WLF-like glass process. Additionally, there is an Arrhenius-like process (4). The points (△, ▲) are calculated from dynamic calorimetry measurements of the glass transition region (Fig. 4).

spatial limitation appears. Therefore the straight line 4 in Fig. 2 (Arrhenius) will change to WLF behavior at higher temperatures.

Because of the thermal stability (melting) of the structure under investigation it is not possible to observe this change for this sample. So we looked for samples with a crystalline structure (dimension of the amorphous regions) such that the change from Arrhenius to WLF behavior can be observed inside the frequency window available (10^{-3} to 10^{7} Hz). Results of preliminary calorimetry studies are presented in this paper. Results from dielectric investigations will be published elsewhere [6].

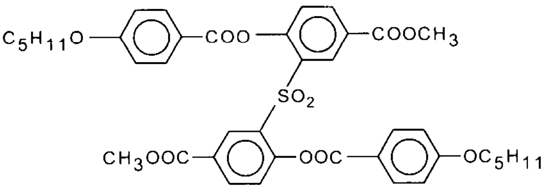

Fig. 3. Compound A: 3,3′-sulfonylbis[methyl 4-(4-*n*-pentyloxybenzoyloxy)benzoate].

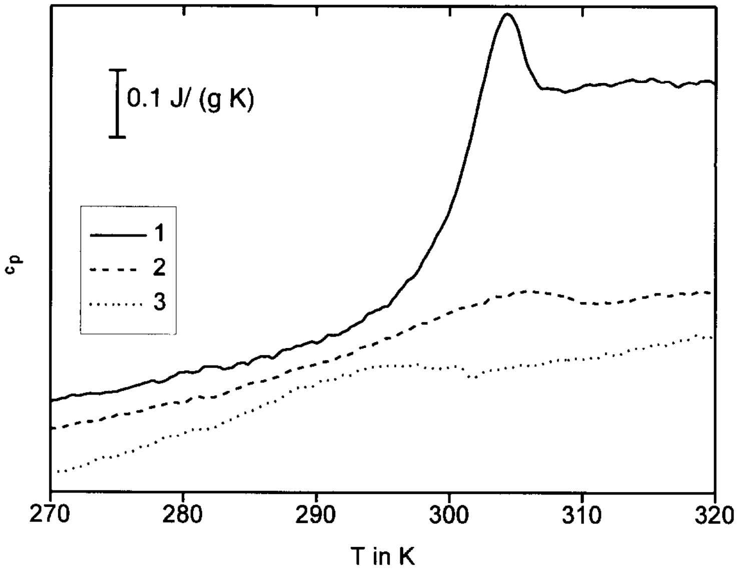

Fig. 4. Thermograms of the compound A in the glass transition region: 1, nematic; 2, after crystallization (2 h at 310 K); 3, after crystallization (13 h at 310 K).

EXPERIMENTAL

The liquid crystals studied are 3,3′-sulfonylbis[methyl 4-(4-*n*-pentyloxybenzoyloxy)benzoate] (compound A, Fig. 3) and 3,3′-sulfonylbis[(4-nitrophenyl) 4-*n*-hexyloxybenzoate] (compound B, Fig. 5). These compounds show a nematic phase which appears only when supercooling the isotropic melt, because the melting points ($T_{mA} = 443$ K; $T_{mB} = 451$ K) are higher than the clearing points ($T_{NIA} \approx 432$ K; $T_{NIB} \approx 389$ K).

The appearance of liquid-crystalline properties is an interesting phenomenon for this molecular structure, because there are two mesogenic phenyl benzoates ligated as rod-like rigid molecular halves by a sulfonyl group, forming a “siamese twin” mesogen.

The synthesis of compound A is possible by a simple three-step procedure starting from methyl-4-hydroxybenzoate [7]. A scheme for the preparation of compound B is given in the literature [8]. The crude products are recrystallized from methanol five times. We obtained flat

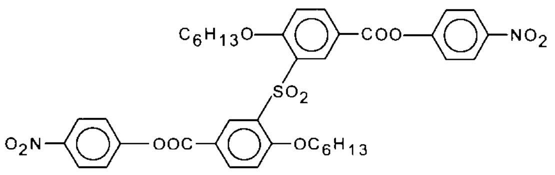

Fig. 5. Compound B: 3,3′-sulfonylbis[(4-ntriophenyl) 4-*n*-hexyloxy-benzoate].

plates (about $0.5 \times 0.3 \times 0.1\ mm^3$). By means of several investigation methods the antiparallel conformation of both molecular halves in the nematic state could be proved [9].

The calorimetric experiments were carried out with a computer controlled Perkin-Elmer DSC-2 [10]. The sample mass was about 5 mg (Sartorius MP500), the heating rate $20\ K\ min^{-1}$ and the cooling rate $80\ K\ min^{-1}$ to get nematic glasses. The samples were crystallized inside the calorimeter. After annealing, the samples were cooled at a rate of $20\ K\ Min^{-1}$ to minimize enthalpy relaxation effects in the following heating run with the same rate.

The purge gas was nitrogen and the heat sink was cooled using a cryostat FT900 from Julabo. The temperature of the heat sink was 230 ± 0.1 K, electronically controlled. To obtain reproducible results the calorimeter and also the cooling system was working at least for 2 days to reach stationary conditions before measuring the base line. The calorimeter was temperature calibrated with indium and lead and the heat flux using a saphire single crystal according to the GEFTA recommendations [11, 12]. The calibration was standardized using copper. Compared with c_p values from adiabatic calorimetry [13], the deviation is less than 1%.

A general view concerning the crystalline structure was obtained by raster electron microscopy (DSM 960; Zeiss). For this, the sample inside the sample pan (without cover) was coated with a thin sputtered aluminum film to prevent electrostatic effects.

RESULTS

Compound B shows the typical relaxation behavior of a glass-forming liquid. In the nematic and in the semicrystalline state we can observe a curved WLF like glass process. In Fig. 6 the thermograms in the transformation interval are shown for samples of different degree of crystallinity. In all cases, a normal glass transition can be seen and we observe a shift of the glass transition temperature to higher values with increasing crystallinity. This is the same behavior that we found for PETP [14]. It can be explained by a slight spatial limitation of the molecular motions due to the crystalline structure.

If we are right that the crystalline structure realized in compound A results in a strong spatial limitation of the glass transition and the crystalline structure realized in compound B result in a slight spatial limitation of the glass transition, then it should be possible to get a crystalline structure between these boundaries by mixing the compounds. Because both compounds form nematic phases it is possible to mix them in the liquid phase. The compounds were mixed in a sample pan by melting the mechanically mixed powder inside the calorimeter. First results from calorimetric investigations of such mixtures are presented here.

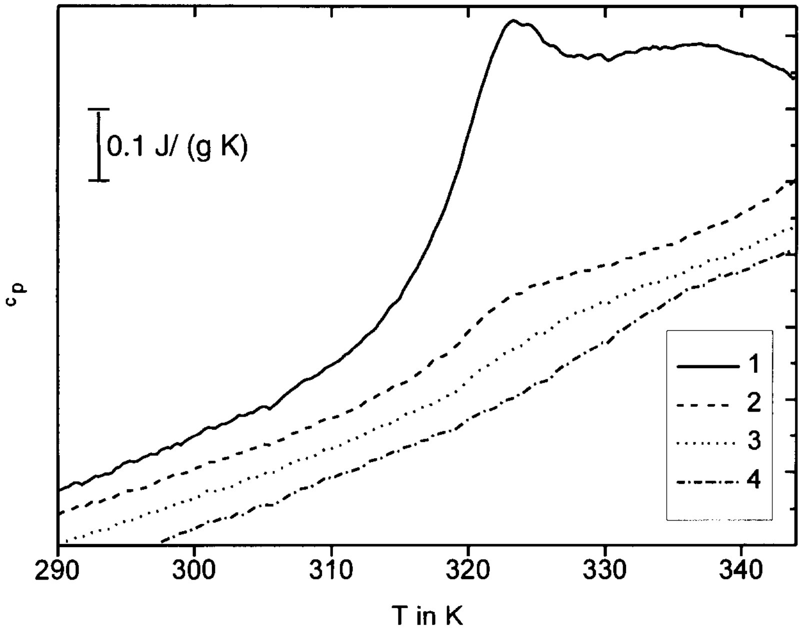

Fig. 6. Thermograms of the compound B in the glass transition region: 1, nematic, α = 0%; 2, after crystallization (20 min at 350 K), α = 63%; 3, after crystallization (120 min at 350 K), α = 79%; 4, after crystallization (320 min at 350 K), α = 88%.

At first we looked at whether the compounds form good mixtures. In Fig. 7 the thermograms after quenching from the melt (80 K $\min^{-1}$) for a 50:50 mixture of compounds A and B and for the pure compounds are shown. The crystallization and melting behavior of the pure compounds is very complex and shows some polymorphism. For the mixture, we can not observe any crystallization or melting. Annealing the 50:50 mixture at different temperatures for various times also results in samples without crystallinity.

Nevertheless there are some arguments for mixing of both compounds in the thermogram of the mixture.

(i) The glass transition of the mixture is between the glass transitions of the pure compounds.

(ii) Only one clearing point is observed for the mixture in the region of 425 K.

(iii) No crystallization or melting of a pure component can be seen in the thermogram of the mixture.

Because compound B dominates the properties of the mixture it was necessary to use mixtures with a very small content of compound B. In the following we will discuss the behavior of the mixture of compounds A:B = 94:6. In Fig. 8 the thermograms of this mixture after annealing at 335 K for different times are shown. With increasing annealing time the exothermic crystallization peak around 380 K decreases and also the

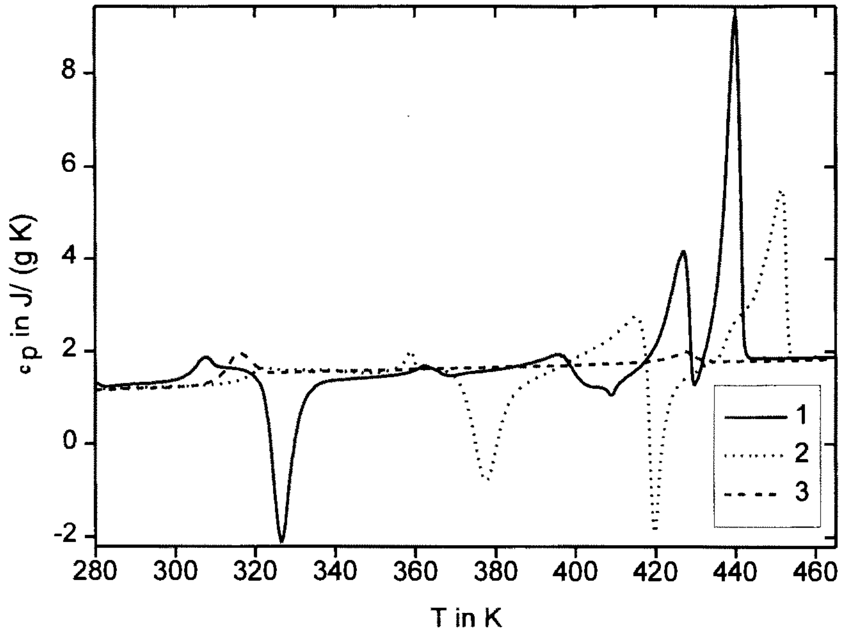

Fig. 7. Thermograms of the compound A (1), B (2) and the mixture of compounds A:B = 50:50 (3) after cooling at 80 K min^{-1}.

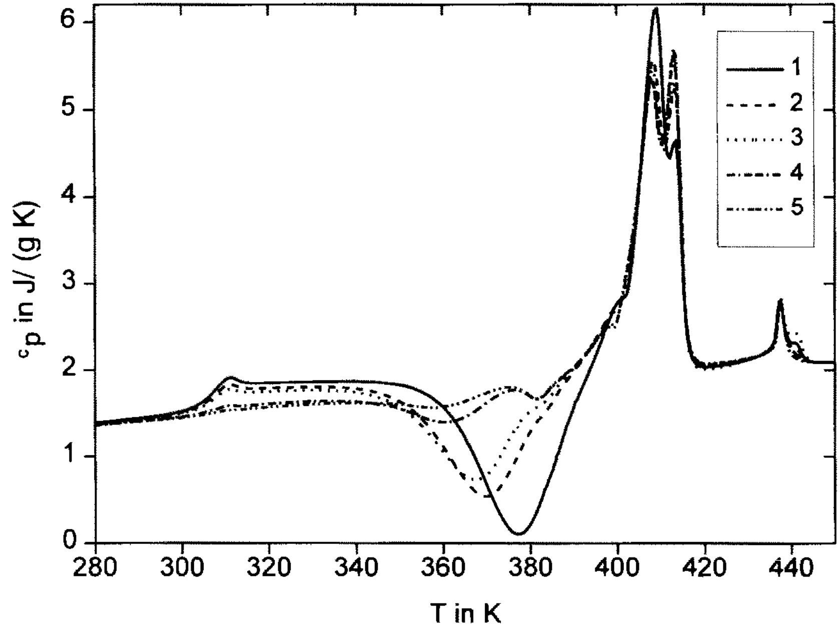

Fig. 8. Thermograms of the mixture of compounds A:B = 94:6: 1, after crystallization (5 min at 335 K), $\alpha = 9\%$; 2, after crystallization (20 min at 335 K), $\alpha = 13\%$; 3, after crystallization (25 min at 335 K), $\alpha = 38\%$; 4, after crystallization (40 min at 335 K), $\alpha = 76\%$; 5, after crystallization (45 min at 335 K), $\alpha = 86\%$.

intensity (step height Δc_p) of the glass transition decreases. Between 430 and 440 K we observe a very complicated transition from liquid crystalline to the isotropic state, as we can also see from thermo-optical investigation. The peak area and the structure of the peak depends on the thermal history of the sample (see Figs 8 and 10).

From compounds A and B we know that they crystallize as a simple two phase system (crystalline and nematic phase only). We checked this by comparing the increase of the crystalline fraction (increase of the heat of fusion $\Delta_m H$) with the decrease of the nematic fraction (decrease of the step height of the glass transition Δc_p) [15]. In the case of a two phase system we found a straight line with the slope −1 for $\Delta c_p/\Delta c_{pa} = f(\Delta_m H/\Delta H_0)$ where Δc_{pa} stands for the step height of the nematic and ΔH_0 for the heat of fusion of the 100% crystalline samples. For the pure compounds, we can prepare samples with 100% and with 0% crystalline fraction [4]. In the case of the pure compounds we are able to verify the dependence over the whole range of crystallinity. The slope of −1 means that the pure compounds crystallize as a two phase system. This behavior allows us to determine the heat of fusion ΔH_0 for a 100% crystalline mixture which we can not produce by annealing. In Fig. 9 the behavior of the mixture of compounds A:B = 96:4 is presented. The heat of fusion for the 100% crystalline mixture results in 51 J g^{-1}. This value is used to determine the degree of crystallinity by $\alpha = \Delta_m H/\Delta H_0$.

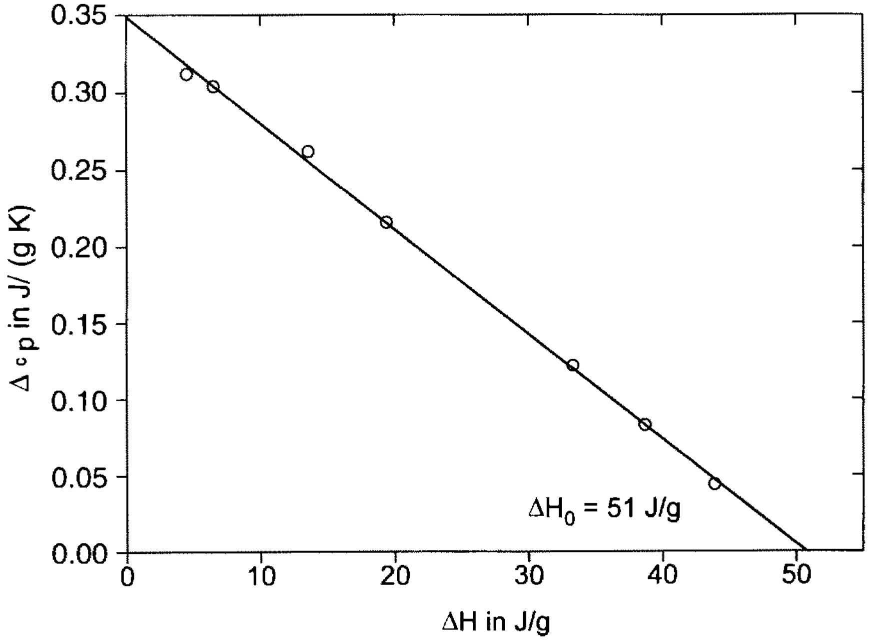

Fig. 9. The step hight of the specific heat capacity Δc_p versus the heat of fusion $\Delta_m H$ for the mixture of compounds A:B = 94:6. The crystallization temperature is 335 K. The extrapolation results for the 100% crystalline state in $\Delta H_0 = \Delta H(\Delta c_p = 0) = 51$ J g^{-1}.

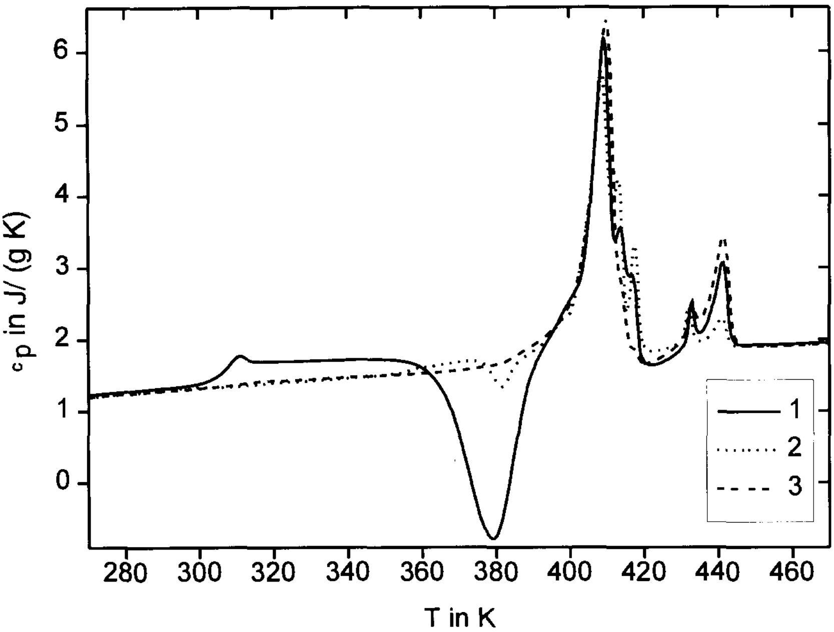

Fig. 10. Thermograms of the mixture of compounds A:B = 94:6: 1, nematic, $\alpha = 0\%$; 2, after crystallization (1 h at 350 K), $\alpha = 91\%$; 3, after crystallization (1 h at 380 K), $\alpha = 98\%$.

The aim of this work is to find the change from a slightly to a strongly hindered glass transition. Therefore, we studied samples annealed at different temperatures for times long enough to produce the maximum degree of crystallinity (less than 100%) for the crystallization temperature used. Figure 10 shows the thermograms of the mixture after annealing for 1 h at different temperatures. In the range 360–390 K we observe that annealing at various temperatures results in different crystalline structures. In Fig. 11 the thermograms in the glass transition interval of the mixture are presented. There we can observe both types of curves we discussed above. After annealing for 1 h at 350 K we see a broader glass transition interval which is shifted to a higher glass temperature. We find the same effects for PETP and compound B. The crystalline structures of these samples result in a weak spatial limitation of the glass transition. After annealing for 1 h at 380 K we observe the same "peak" at lower temperatures compared with the glass temperature of the nematic liquid as seen for compound A. That means the crystalline structure yields a strong spatial limitation of the glass transition. So we are able to produce by annealing with one sample different crystalline structures which result in a weak or a strong spatial limitation of the thermal glass transition. If this is right we have to determine the dimension of the amorphous regions in the samples and we can approximate the minimal volume which is necessary for a co-operative thermal glass transition.

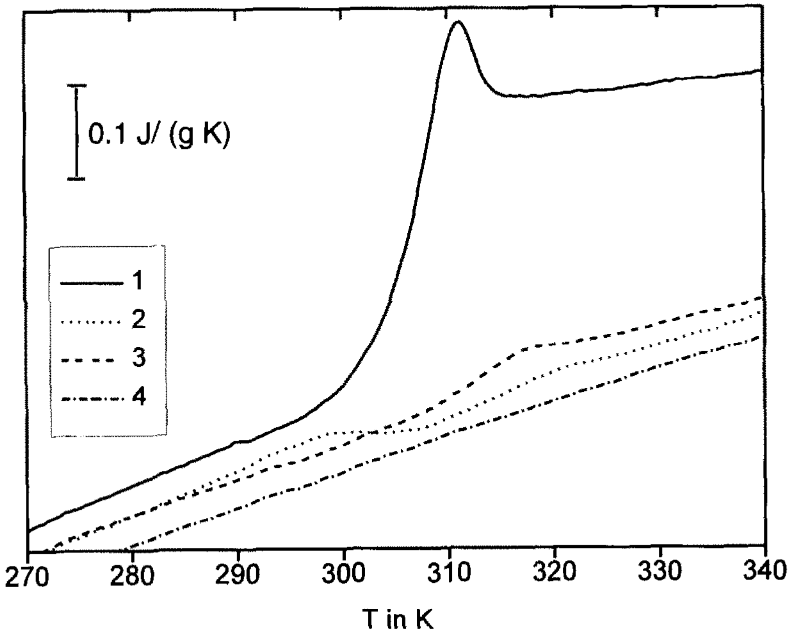

Fig. 11. Thermograms of the mixture of compounds A:B = 94:6 in the glass transition region: 1, nematic, $\alpha = 0\%$; 2, after crystallization (1 h at 350 K), $\alpha = 91\%$; 3, after crystallization (1 h at 380 K), $\alpha = 98\%$; 4, compound A crystallized from ethanol solution, $\alpha = 100\%$.

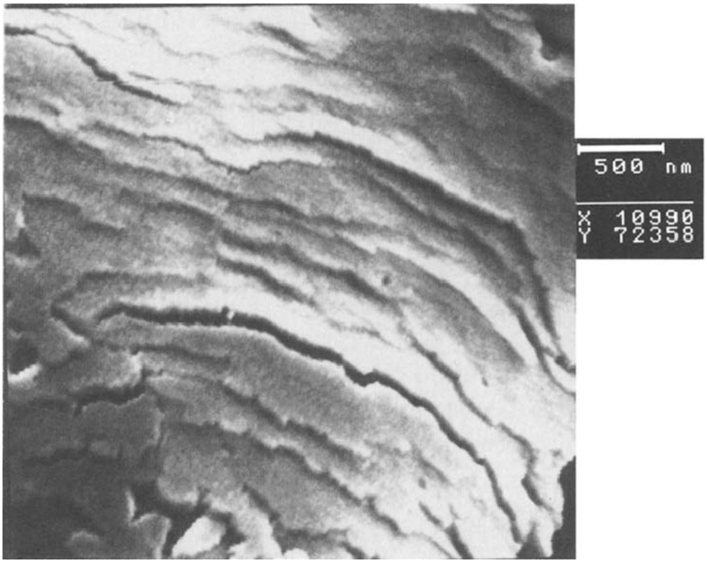

Fig. 12. Electron micrograph of the mixture of compounds A:B = 94:6 after crystallization (240 min at 335 K).

Therefore we need to study the structure of the samples. The first information we present is from raster electron microscopy as shown in Fig. 12. We observe some lamellae like structures which we will investigate further by X-ray diffraction.

DISCUSSION

Predictions about typical length scales associated with the glass transition from different models [16–19] result in values of some nanometers. A direct experimental verification in the equilibrium is, at present, not possible, so we tried to use indirect experimental methods to estimate the characteristic length scales. It is possible to obtain information on typical length scales of the glass transition by the study of the relaxation behavior of small amorphous layers.

The results presented here show that it is possible to observe the breakdown of the co-operative molecular motions related to the thermal glass transition by variation of the crystalline structure of a semicrystalline sample. Because there are no quantitative data concerning the structure and the dimensions of the amorphous parts inside the semicrystalline structure, we cannot compare it with the breakdown of the co-operative glass transition. Therefore we will try to get further information on the crystalline structure and we will perform dielectric investigations in a wide frequency range to observe the change from co-operative to non-co-operative behaviour.

ACKNOWLEDGMENTS

The authors express their thanks to B. Stoll (Ulm) for helpful discussions. A. Roger (Rostock) for the preparation of the liquid crystalline compounds, and to the Deutsche Forschungsgemeinschaft for financial support.

REFERENCES

1 Proceedings of 1990 International Discussion Meeting on Relaxation in Complex Systems, J. Non-Cryst. Solids, 131–133 (1991).
2 J. Jäckle, Rep. Progr. Phys., 49 (1986) 171.
3 C. Schick and E. Donth, Phys. Scr., 43 (1991) 423.
4 C. Schick, B. Stoll, J. Schawe, A. Roger and M. Gnoth, Progr. Colloid Polym. Sci., 85 (1991) 148.
5 E.J. Donth, Relaxation and Thermodynamics in Polymers. Glass Transition. Akademie Verlag, Berlin, 1993.
6 U. Koy, Progr. Colloid Polym. Sci., in preparation.
7 H. Dehne, A. Roger, D. Demus, S. Diele, H. Kresse, G. Pelzl, W. Wedler and W. Weissflog, Liquid Crystals, 6 (1989) 47.

8 A. Roger and H. Dehne, Wiss. Z. Päd. Hochsch. Güstrow, Math.-Naturwiss. Fak., 29 (1991) 83.
9 U. Baumeister, H. Hartung, A. Roger and H. Dehne, Mol. Cryst. Liq. Cryst., 214 (1992) 33.
10 W. Winter and G.W.H. Höhne, Thermochim. Acta, 187 (1991) 257.
11 G.W.H. Höhne, H.K. Cammenga, W. Eysel, E. Gmelin and W. Hemminger, Thermochim. Acta, 160 (1990) 1.
12 S.M. Sarge, E. Gmelin, G.W.H. Höhne, H.K. Cammenga, W. Hemminger and W. Eysel, Thermochim. Acta in preparation.
13 R.E. Pawel and E.E. Stansbury, J. Phys. Chem. Solids, 26 (1965) 607.
14 C. Schick, J. Wigger and W. Mischok, Acta Polymerica, 41 (1990) 137.
15 S.Z.D. Cheng and B. Wunderlich, Macromolecules, 20 (1987) 1630.
16 E. Donth, J. Non-Cryst. Solids, 53 (1982) 325.
17 W.R. Pechhold and B. Stoll, Polym. Bull., 7 (1982) 413.
18 A.J. Owen and R. Bonart, Polymer, 26 (1985) 1034.
19 U. Strom and P.C. Tailor, Phys. Rev. B, 16 (1977) 5512.