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The Glass Transition of *p*-Alkyl-*p'*-Alkoxy-Azoxybenzene Mesophases

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An isomeric mixture of *p*-butyl-*p'*-methoxy-azoxybenzenes (IV) and the low melting eutectic mixture of *p*-butyl-*p'*-methoxy-azoxybenzenes with *p*-ethyl-*p'*-methoxy-azoxybenzenes (V) have been analyzed with differential scanning calorimetry (DSC). By quenching, it was possible to establish the glassy mesophase of both materials. Their glass transition temperatures are 207.6 K and 208.1 K, respectively, with an increase in heat capacity at T_g of 129 JK^{-1} mol^{-1} and 102 JK^{-1} mol^{-1}. As found previously with polymeric mesophases, the hysteresis is strongly reduced, while the ΔC_p seems little affected by going from an amorphous glass to a mesophase glass. The melting, cold crystallization, and mesophase-isotropic melt transitions were also studied.

1 INTRODUCTION

The glass transition is well understood as an upper temperature limit to the solid, amorphous phase. Above the glass transition temperature, micro-brownian motion characteristic of a liquid becomes possible.

Very little information is available about the glass transition in mesophase materials which are unable to crystallize on cooling. Such inability to crystallize is frequent is macromolecular mesophase materials. To study the glass transition in macromolecular mesophases, we analyzed poly(acryloyloxybenzoic acid), PABA, which could be obtained both, as an amorphous glass and as a mesophase glass.[1] The mesophase glass had a substantially higher glass transition temperature than the amorphous glass (408 K instead of 348 K), but approximately the same ΔC_p (43 JK^{-1} mol^{-1} instead of 39 JK^{-1} mol^{-1}). Since in PABA the mesogenic group is a side-group attached to the backbone chain, we also looked at a main chain mesogenic macromolecule, a copolyester of

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ethylene terephthalate and oxybenzoate, PET-co-OB. In this case only the mesophase glass could be made.[2] Again, the ΔC_p was comparable to the copolyesters which show no mesophase behavior, and the temperature of the glass transition indicated no abnormal rise when going from mesophase copolymer compositions to the amorphous compositions. All mesogenic glasses showed a distinct reduction in the heat capacity hysteresis behavior. Hysteresis is found for all amorphous glasses (i.e. a slowly cooled glass develops a sizeable endotherm in the glass transition region when heated fast).[3]

In the present paper we present work on the thermal properties of low molecular weight mesophase materials to make comparisons with the macromolecular materials. We found that some of the *p*-alkyl-*p'*-alkoxy-azoxybenzenes and their eutectic mixtures can be prevented from crystallization by quenching. These materials were originally synthesized because of their low temperature mesophase.[4] Thermal analysis and optical microscopy were the analysis techniques of choice.

2 EXPERIMENTAL

The two samples investigated were obtained from E. Merck, Darmstadt (U.S. supplier: E. M. Laboratories, Elmsford, N.Y.). They are sold as "Nematic Phase IV, (17/76) Licristal" article number 10,105, and "Nematic Phase V, (-5/75) Licristal" article number 10,206. The numbers in parenthesis give the transition temperatures in °C from crystal to nematic phase and from nematic phase to isotropic melt. Sample IV is *p*-butyl-*p'*-methoxy-azoxybenzene (molar mass 0.2844 kg) in the normal mixture of isomers of azoxybenzenes (about 60:40). Sample V is a eutectic mixture of 65 wt.-% *p*-butyl-*p'*-methoxy-azoxybenzene and 35 wt.-% *p*-ethyl-*p'*-methoxy-azoxybenzene (molar mass 0.2746 kg), both in their normal mixtures of azoxybenzene isomers. The synthesis of the compounds is described in Ref. 4. The physical properties have been summarized by Knaak *et al.*[5]

Thermal analysis was performed with a duPont 990 Thermal Analyzer coupled to a 910 DSC-module. For differential scanning calorimetry (DSC) every sample was heated to 400 K to reach the liquid state, then cooled to the solid state with a programmed rate to 160 K, to impart a fixed thermal history.[6] DSC traces were subsequently taken on renewed heating of the sample with a standard heating rate of 50 K min^{-1}. The temperature scale was corrected for instrument lag by calibration with high purity standard materials (*n*-octane, *n*-decane, *n*-dodecane, *p*-nitrotoluene, naphtalene, benzoic acid and indium).[7] The heats of transition were calibrated with the same standard substances. All DSC measurements were run under nitrogen atmosphere.

Glass transition temperatures, T_g, are taken at the temperature of half unfreezing, a procedure which gives reproducible values as long as there is no

excessive hysteresis peak. The increase in heat capacity at the glass transition, ΔC_p, was evaluated by comparison with the heat capacity of sapphire.[8] The other transition temperature, i.e.: the beginning of crystallization, T_c, the beginning of melting, T_m, and the mesophase-isotropic transition temperature, T_{mes}, were evaluated by extrapolation of the peak on the low temperature side in a straight line to the extended baseline. The peak temperature of the crystallization exotherm, T_p, was read directly from the position of the peak on the temperature scale.

The heats of transition, i.e.: heat of crystallization ΔH_c, heat of fusion ΔH_m, and heat of mesophase transition ΔH_{mes}, were calculated from the area underneath the endotherm or exotherm.

3 RESULTS AND DISCUSSION

The samples cooled at specific cooling rates were analyzed between 160 to 400 K. In this temperature region at most four transitions occurred when going from low to high temperature: the glass transition, a cold crystallization exotherm, the melting peak and the mesophase-isotropic melt transition. The studied transitions were characterized by the following parameters: T_g, ΔC_p at T_g, temperature of the beginning of crystallization, T_c, the peak of the exotherm, T_p, the melting temperature, T_m, mesophase transition temperature, T_{mes}, and the heats of transition ΔH_c, ΔH_m and ΔH_{mes}.

In Figure 1 typical DSC curves of sample IV are shown. From the traces it can be seen that the cooling rate influences the character of the samples in their low temperature behavior. A sharp glass transition is seen only for samples cooled at 50 and 20 K min^{-1}. A cooling rate of 10 K min^{-1} causes considerable broadening of the glass transition. The samples cooled at 5 K min^{-1} and less have practically no glass transition. These changes are connected with the crystallization of the sample during the imparting of the thermal history. Slowly cooled samples crystallize almost fully and have thus no glass transition. Fast cooled samples crystallize only partially. This interpretation is born out by the crystallization behavior above the glass transition region. The more glassy the material, the larger is the cold crystallization exotherm. Cold crystallization is the term used to distinguish crystallization on heating from the normal crystallization which is carried out on cooling.[9]

The melting peaks and mesophase to isotropic liquid transition peaks are practically the same for all measured samples, i.e. cold crystallization erases all imparted thermal history. The quantitative data characterizing the transitions of Sample IV are reported in Table I. From this table the correlation between glass transition and crystallinity of the sample can be seen. In the last column the weight fraction crystallinity w^c at T_g, calculated from the differences in heats of crystallization and heats of melting is reported. One can say that

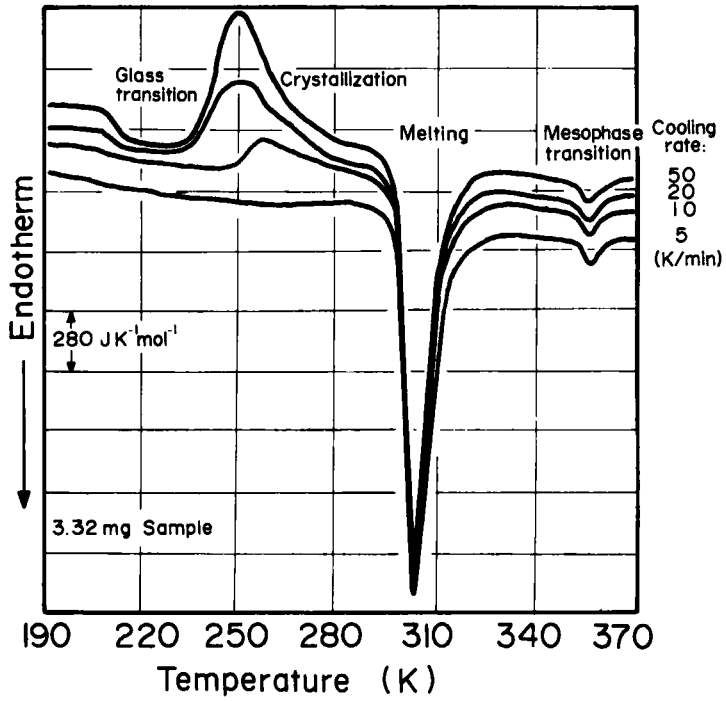

FIGURE 1 DSC curves of Sample IV, *p*-butyl-*p'*-methoxy-azoxybenzene heated at 50 K min^{-1}. (Cooling rates are indicated in the graph).

every sample with a strong glass transition is only partially crystalline. Efforts to reach a completely amorphous samples were not successful. Even quenching in liquid nitrogen does not produce a fully amorphous sample (Sample A). Its crystallinity is similar to the sample cooled at 50 K min^{-1}, but the crystallization process on heating shows differences. The crystallization peak consists in this case of four irregular subpeaks, which suggests the possibility of organizing the material into different metastable crystals. The dominant crystallization peak occurs at a temperature of 220 K when one heats the sample at 50 K min^{-1}. This explains why the Sample B, which was quenched from 400 K to 230 K, a temperature below the main crystalline peak of the other samples, and then slowly cooled (2 K min^{-1}) to 160 K, was actually more crystalline than the more slowly crystallized samples, and could not serve for a study of hysteresis phenomena. At 220 K, crystallization occurred and only a broadening of glass transition is observed which is common for partially crystallized samples consisting of very small crystals.

The mesophase-isotropic liquid transition temperature, T_{mes}, and the melting temperature, T_m, as measured by us (averages 352.5 ± 1.0 K and

TABLE I

Quantitative data of transitions of *p*-butyl-*p'*-methoxy-azoxybenzene heated at 50 K min^{-1} (Sample IV).

Cooling rate (K min^{-1})	T_g (K)	ΔC_p at T_g ($JK^{-1}mol^{-1}$)	T_c (K)	T_p (K)	ΔH_c (Jg^{-1})	T_m (K)	ΔH_m (Jg^{-1})	T_{mes} (K)	ΔH_{mes} (Jg^{-1})	w^c at T_g
50	207.4	111.44	238.0	251.3	36.34	298.1	44.88	353.8	1.997	0.19
20	205.6	66.06	233.9	251.3	24.66	297.5	49.07	352.4	1.997	0.49
10	—	—	246.9	256.5	3.68	297.1	45.55	352.6	1.830	0.92
5	—	—	—	—	—	296.0	48.48	352.4	2.098	1.00
A	209.9	95.08	220.1	226.9†	32.94	292.8	41.99	351.0	1.786	0.21
B	—	—	239.6	245.9	10.93	296.3	42.82	352.5	1.964	0.74

A—Sample quenched from 403 K in liquid nitrogen and heated at 50 K min^{-1}.
B—Sample quenched from 403 K to 230 K, slowly cooled at 2 K min^{-1} to 160 K and then heated at 50 K min^{-1}.
† This sample had multiple crystallization peaks. The other peak temperatures were 243.3 K, 254.8 K and 260.9 K.

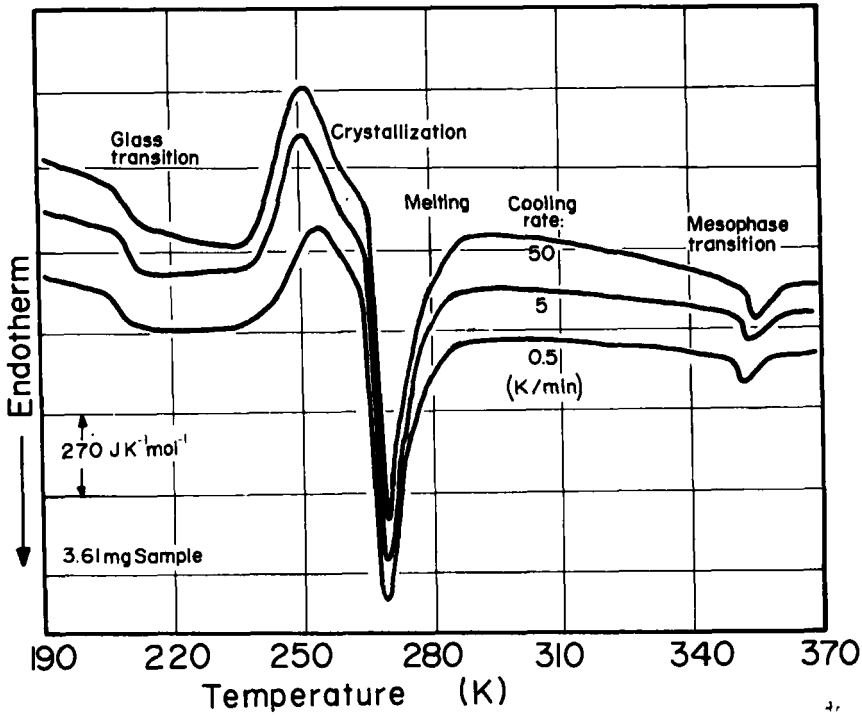

FIGURE 2 DSC curves of Sample V, a eutectic mixture of *p*-butyl-*p'*-methoxy-azoxybenzene and *p*-ethyl-*p'*-methoxy-azoxybenzene, heated at 50 K min^{-1} (cooling rates are indicated in the graph).

296.5 ± 2 K, respectively) are in good agreement with these values reported earlier[4,5] when considering the fast heating rates.

The DSC traces of the differently cooled eutectic mixtures, sample V, are all quite similar. For every cooling rate four rather sharp transitions can be seen. In Figure 2 some of the curves are shown as examples. The crystallization peaks are immediately followed by the melting peaks. This causes some difficulties in the construction of the baseline for the peak area measurements and indicates a much greater hindering to crystallization for the eutectic.

The quantitative data for this sample are reported in Table II. From these data one can see that the thermal history does in this case produce no effect on the temperatures of any of the transitions. Also, the heats of the mesophase-isotropic transitions ΔH_{mes} are not affected. The heats connected with the crystallization processes, however, are dependent on the cooling rate. Faster cooled samples (50, 20 and 10 K min^{-1}) do not crystallize at all on cooling, and there is even only partial crystallization during heating ($\Delta H_c = \Delta H_m$, but a low value of ΔH_m). Occasionally a sample did not crystallize at all on heating

TABLE II

Quantitative data of transitions of the eutectic mixture of *p*-butyl-*p'*-methoxy-azoxybenzene with *p*-ethyl-*p'*-methoxy-azoxybenzene heated at 50 K min^{-1} (Sample V).

Cooling rate (K min^{-1})	T_g (K)	ΔC_p at T_g ($JK^{-1}mol^{-1}$)	T_c (K)	T_p (K)	ΔH_c (Jg^{-1})	T_m (K)	ΔH_m (Jg^{-1})	T_{mes} (K)	ΔH_{mes} (Jg^{-1})	w^c at T_g
50	209.3	106.94	244.0	260.0	16.31	269.6	15.38	350.3	1.628	0
20	207.8	99.79	246.5	260.7	12.39	269.0	11.30	350.7	1.742	0
10	206.9	98.63	247.5	254.2	17.62	269.0	17.12	349.7	1.838	0
5	207.4	109.11	242.7	253.6	17.67	268.1	18.17	349.7	1.612	0.02
2	209.5	96.79	240.6	253.0	17.29	270.6	25.92	349.6	1.775	0.34
1	208.4	96.57	243.8	261.9	11.64	268.9	13.86	349.1	1.704	0.16
0.5	207.1	93.04	244.8	258.8	14.07	266.7	18.42	348.9	1.775	0.24
C	208.8	102.11	—	—	0	—	0	349.7	1.707	0
D	206.9	34.24	232.4	254.0	1.59	266.9	34.33	349.3	1.727	0.95

C—Sample did not crystallize, preliminary cooling at 20 K min^{-1}.
D—Sample crystallized 60 min at 265 K, then cooled to 163 K (2 K min^{-1}) and heated 50 K min^{-1}.

(Sample C). The heats of fusion never reached the values of Sample IV (see Table I). Even a sample annealed at 265 K (Sample D) did not crystallize fully. Some crystallization of Sample V occurs while cooling at low cooling rates (2, 1 and 0.5 K min^{-1}). Again, the total level of crystallinity reached is not very reproducible and seems to depend on accidental nucleation conditions. The mesophase-isotropic transition temperatures, T_{mes}, and the melting temperature T_m as measured by us (averages 349.7 ± 0.6 K and 268.6 ± 1.3 K, respectively) are in good agreement with these values reported earlier[4,5] when considering the fast heating rates.

In Figure 3 micrographs of the samples quenched from 400 K in liquid nitrogen are shown. The pictures were taken immediately after removing the glass slides from the liquid nitrogen, i.e. at a temperature below T_g. Anisotropic, birefringent domain structures, typical for liquid crystals can be seen. The smaller domain size of Sample IV when compared to Sample V is probably the result of its partial crystallinity. Heating the samples above their T_g involves some changes of interference colors inside the domains due to cold crystallization. Above T_m, both color and domain size changes are observed (mainly in Sample IV).

To find a reliable value for the heat of fusion of *p*-butyl-*p'*-methoxy-azoxybenzene (Sample IV), the first four values of Table I were averaged. On a molar basis, the heat of fusion is 13.4 ± 0.6 kJ mol^{-1}, which leads to an entropy of fusion of 45.2 JK^{-1} mol^{-1}. For the transition to the isotropic phase the corresponding values are averaged over all data: $\Delta H_{mes} = 0.55 \pm 0.03$ kJ mol^{-1} and $\Delta S_{mes} = 1.6$ JK^{-1} mol^{-1}. The total entropy change on fusion is thus 46.8 JK^{-1} mol^{-1}, a value which agrees with the average of typical rigid molecules which gain positional and orientational freedom on fusion[10] (30–50 JK^{-1} mol^{-1}). The pending alkyl and alkoxide groups seem to contribute little to the entropy of fusion. The heat of fusion and entropy of fusion of the eutectic, Sample V, is expected to be only little different from Sample IV. Their lower values are most likely indicative that even Sample D of Table II is not fully crystallized. The heat and entropy of transition to the isotropic phase does not vary from sample to sample (0.47 ± 0.02 kJ mol^{-1}, 1.35 JK^{-1} mol^{-1}) and is close to that of Sample IV, an indication that the mesophase involves all the sample and not only the prior crystallized parts. A similar observation was made in macromolecular samples.[1,2] While crystallization leads to semicrystalline samples, mesophase formation involves all matter.

The final results involve the glass transition. In this case the Samples V of the eutectic are analyzed most easily. The indication is that ΔC_p at T_g, as well as T_g itself, are close for both samples. ΔC_p for the eutectic was averaged for the four completely amorphous samples and gave a value 101.9 ± 3.7 JK^{-1} mol^{-1} at 208.1 ± 1.0 K. The glass transition temperature was averaged over all samples. For the Samples IV, which crystallized completely after the glass transi-

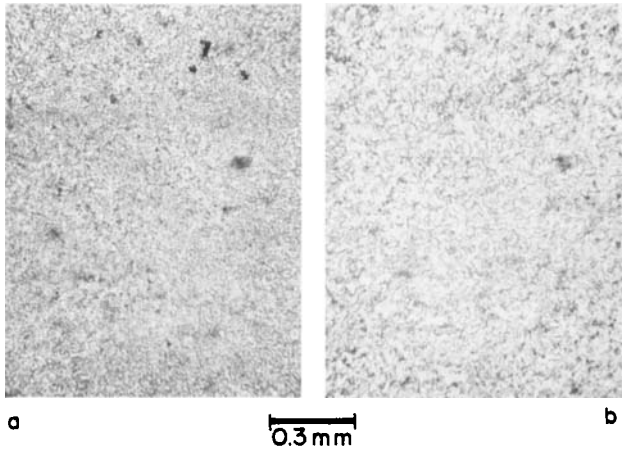

FIGURE 3 Micrographs of the samples quenched from 400 K in liquid nitrogen below the glass transition temperature (crossed polaroids). (a) Sample IV, *p*-butyl-*p'*-methoxy-azoxybenzene (b) Sample V, a eutectic mixture of *p*-butyl-*p'*-methoxy-azoxybenzene and *p*-ethyl-*p'*-methoxy-azoxybenzene.

tion the values for ΔC_p are less accurate. The three ΔC_p-values were averaged after correction for the weight fraction crystallinity below the glass transition temperature. ΔC_p for *p*-butyl-*p'*-methyoxy-azoxybenzene is 129 ± 9 JK^{-1} mol^{-1} at 207.6 ± 2.1 K. Using the rule of constant ΔC_p per rigid backbone unit[11,12] suggests that all seven rigid units per molecule gain mobility on devitrification, with a slightly lower number for the eutectic sample, which has somewhat shorter pending groups (small rigid units have a ΔC_p of 11.3 JK^{-1} mol^{-1}, phenylene groups about 20 JK^{-1} mol^{-1}). Overall, ΔC_p is thus similar to the expected value for a completely amorphous glass. The actual state of the glass was, however, a mesophase, proven by the birefringence of all glassy samples as shown in Figure 3. Furthermore, we found that changes in cooling as well as heating rate did not affect the mesophase to isotropic phase transition, which means that fast quenching does not permit a vitrification of the isotropic liquid. The glass transition is thus a transition of the solid mesophase. In contrast to the melting transition, which shows no contribution from the flexible end-groups, the glass transition reveals a major contribution from the flexible end groups. Checking into the hysteresis behavior at the glass transition, we find (particularly for the fully glassy eutectic Samples V) that even if cooling and heating rates differ by a factor 100 there is *no* indication of hysteresis. The same observation was made for macromolecular mesophases.[1,2] It must mean that the glass transition of mesophases is much less temperature dependent than of amorphous glasses.

4 CONCLUSIONS

The study of the low molecular weight *p*-alkyl-*p'*-alkoxy-azoxybenzene mesophases revealed their glass transition temperatures with a ΔC_p close to a value expected for amorphous materials with frozen mobile pending groups in the glassy state. The absence of the hysteresis for differences between heating and cooling rates of 100 indicates a largely time-independent glass transition temperature. All these observations are similar to the observations made on macromolecular mesophases.[1,2] The overall melting entropy reveals little conformational entropy contribution from the pending groups, suggesting that they have gained internal rotation below the melting temperature. One might expect that the pending groups may have more conformational entropy in the crystal than in the glass.

Acknowledgments

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