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THERMAL ANALYSIS OF THE CONFORMATIONAL DISORDER IN SCLC POLYMERS WITH RIGID BACKBONE

Glass transition studies

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Abstract

Bis [(ω-(4'-cyanobiphenyl)-4-yl)oxy-*n*-alkyl]norborn-5-ene-2,3-dicarboxylate was polymerised via ring opening metathesis polymerisation (ROMP). Two disubstituted polynorbornene derivatives both of *cis* configuration with different length of the side-chain were studied. Differential scanning calorimetry (DSC) was used to study the effect of thermal history on the assignment of the glass transition event associated with the biaxial orientation of a smectic phase. Glass transition temperatures, the change of isobaric specific heats at T_g and the enthalpies of isotropisation were calculated. The DSC traces only show the classic step-wise change in T_g in some cases, giving the evidence that the amorphous domains are constrained and highly restricted in movement due to the morphology developed as a result of the biaxial stretching. Based on the literature data of mono- and disubstituted polynorbornene derivatives and our calorimetric experiments, the shape of T_g dependence on number of (CH_2) units is interpreted. The origin of this shape is discussed.

Keywords: DSC, glass transition, side-chain liquid crystal polymer (SCLC)

Introduction

The glass transition seems to be the most common thermal event dealing with polymeric amorphous materials. The studies can become complicated when dealing with oriented, semicrystal or liquid crystal polymers. The fabrication of these kind of polymers into items such as thin films, membranes or fibres often involves a number of processing steps which can impart structural or morphological changes. The detection of glass transition for highly crystalline polymers becomes difficult by DSC since its intensity decreases as a result of increasing crystallinity [1]. The observation of T_g is more difficult for oriented materials which may in fact contain three distinct domains: crystalline, constrained amorphous and unconstrained amorphous [2–5].

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The biaxial orientation coupled with liquid crystalline order of polymer pattern produces a highly pinned morphology in which the amorphous domains are very restricted in their movements. The orientation induced by main- or side-chain liquid crystallinity is not the same and should result in different increases for the glass transition. The side-chain liquid crystal (SCLC) polymers are the specific group of the liquid crystals (LC) for which many studies concerning the influence of a main chain, the length of side chains, the sort of mesogenic groups and tails (with different polarity) attached to the side chain on structure in bulk were performed. Changing at least one of the factors mentioned above can drastically change polymer supermolecular structure [6–7]. When the number of methylene groups in a side chain is changed, some new polymer pattern is very often created.

The influence of the degree of crystallinity for highly crystallised polymers on the thermodynamic parameters describing the glass transition was found. So, the same should be true of the LC systems. Additionally, the type of a LC structure might affect the behaviour of the amorphous phases. The description of a polymer pattern based on SAXS studies of the disubstituted polynorbornene derivatives was presented earlier [8]. Because, the rigidity of the backbone and the spacer length are two very important limiting factors in the creation of LC phases, the influence of this phase behaviour on an amorphous region (T_g, $\Delta C_p(T_g)$) by changing the spacer length was studied. Based on the literature data of mono- and disubstituted polynorbornene derivatives [9 12], our calorimetric experiments are used to interpret the shape of T_g dependence on CH_2 units number. The origin of this shape is discussed.

Experimental

Sample preparation

The polymer samples were synthesised via ring opening metathesis polymerisation (ROMP) of (±)endo,exo-bis[(ω-(4'-cyanobiphenyl)-4-yl)oxy-*n*-alkyl]norborn-5-ene-2,3-dicarboxylates (with n=6 or 11 methylene groups as the alkylene spacer) according to the procedure described in a previous paper [12]. The initiator was $[Mo(CH\text{-}t\text{-}Bu)(NAr)(t\text{-}BuF_6O)_2$ with Ar=2,6-diisopropylphenyl and BuF_6O=bis(trifluor-methyl)-*t*-butyloxy. This yielded a polymer with a *cis* content s_c=80% as determined by NMR. As the racemic monomer mixture was used, the tacticity of the polymers could not be determined but was considered to be mainly atactic. The purified polymer was used for making the specimen for thermal analysis from melt as given the following example.

Polymers were melted at 160°C and were held at this temperature about 40 min, in all cases. The samples were prepared between two aluminium plates. Although, some data were obtained for the samples melted only on one Al-plate or in bulk. Different cooling regimes were applied from slow to very fast (quenching) one. In this way, bars with thickness varying from 0.8 to 1.0 mm were obtained. For DSC measurements one piece of about 10 mg samples cut from those polymer bars was used. Some samples were annealed at 70°C or 110°C for 24 h. Detailed description of thermal history of the polymer samples is presented in the result section.

Method

The thermoanalytical investigations were carried out with a DSC of Polymer Laboratories STA 625 type under the following conditions: environment – nitrogen atmosphere, flow rate – 50 ml min^{-1}, sample pan – aluminium, reference – empty aluminium pan, sample size – about 10 mg, heating rate – 20°C min^{-1} (40, 10, 5, 2, 0.5°C min^{-1}), calibration procedure – done with indium standard.

The glass transition temperatures (T_g) were taken from the middle point of change in heat capacity. The temperatures of isotropisation (T_i) as the maximum point for each endothermal peak were pointed.

Results and discussion

Two disubstituted polynorbornene derivatives both of mainly *cis* configuration with different length of the side-chain (samples CK(6) and CK(11) with the number of methylene units into the side-chain 6 and 11, respectively) were studied. The influence of thermal history on the creation and stability of the LC structure was described earlier [8]. Therefore, special attention in this paper is paid to differences in thermal behaviour of the amorphous phase resulting from an arrangement induced by mesogens.

Different thermal regimes were applied for the samples preparation and the first heating runs were taken into account. Additionally, the first cooling and the second heating runs were recorded too. The original calorimetric recordings of the heat flow changes of different CK(6) and CK(11) samples are presented in Figs 1a and 1b. As compared with DSC data concerning mono- and disubstituted polynorbornene derivatives published earlier [10–12], the traces presented here seem to be similar only for samples which were cooled down very slowly (0.5°C min^{-1}, with non-linear regime). All of them showed an endothermal peak of a first-order transition recognised as the isotropisation phenomenon confirmed in optical polarising microscope (130°C – was pointed out for CK(11) samples). One can see, the quenching process did not change only the T_g values (decrease of these values is typical behaviour as known from other polymer system very well [1]) but also the shape of DSC curves above $T_g(1)$. In the case of CK(11)I samples quenched from 160°C to room temperature between two aluminium plates the drastic decreasing of specific heat were recorded. It was unexpected, that the enthalpy of isotropisation in that case was the highest and the DSC curves presented above $T_g(1)$ such tendency. The traces were entirely repro-

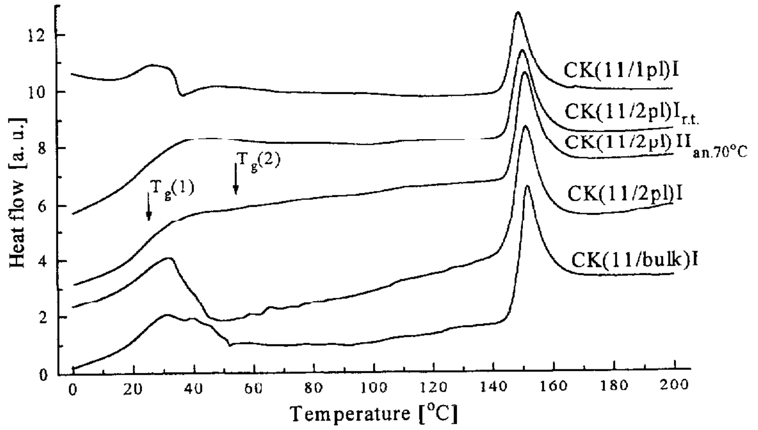

Fig. 1a DSC traces of CK(11) obtained under different thermal history as described in Table 1. The trace at the top was recorded for a sample prepared on 1 plate (1pl) and the one at the bottom for a sample in bulk. The other traces are for samples prepared between 2 plates (2pl)

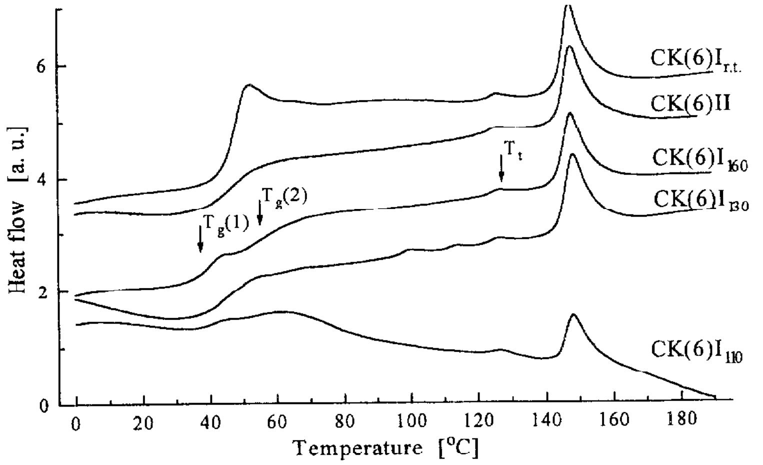

Fig. 1b DSC traces of CK(6) obtained under different thermal history as described in Table 2. The samples were prepared only between 2 plates

ducible and little deviations of the curve shapes were recorded, merely depending on the applied quenching procedures.

CK(11)I samples studied after several days from preparation (stored at room temperature) presented the curves similar to those observed for the samples cooled down very slowly. For the CK(11) samples two second-order phase transitions were observed when they were quenched from lower temperature than T_i or were obtained under slow temperature regime (CK(11)II). The second one was with very low ΔC_p, Table 1. The different DSC traces observed for the sam-

Table 1 Thermodynamic data of CK(11) samples of different thermal history taken from first heating run. The samples were prepared between two aluminium plates. Data in parenthesis were found for the samples prepared on one aluminium plate

Samples	$T_g(1)$/ °C	$\Delta Cp(T_g)$/ kJ (mol °C)$^{-1}$	$T_g(2)$/ °C	$\Delta Cp(T_g)$/ kJ (mol °C)$^{-1}$	T_i/ °C	ΔH_i/ kJ mol^{-1}
CK(11)I	22.3 (20.5)	0.331 (0.341)	– –	– –	151.0 (149.2)	9.99 (8.17)
CK(11)I_{rt}	24.0	0.359	–	–	149.8	8.39
CK(11)I_{a70}	21.9 (21.5)	0.258 (0.361)	39.0 (31.4)	0.036 (0.041)	151.5 (148.7)	7.69 (8.58)
CK(11)I_{a110}	(26.0)	(0.442)	(29.5)	(0.087)	(148.9)	(7.03)
CK(11)II	25.2	0.452	43.0	0.039	150.3	6.94
CK(11)II_{rt}	22.7	0.293	37.0	0.162	149.7	6.94
CK(11)II_{a70}	25.4	0.338	54.5	0.003	150.9	7.27

CK(11)I – sample quenched from 160°C;
CK(11)I_{rt} – sample kept at room temperature during several days;
CK(11)I_{a70} – sample annealed at 70°C over 24 h;
CK(11)II – sample cooling down very slowly in step regime

ples in the temperature range above T_g could be related to changes in the order of the three dimensional structure of the polymer patterns caused by changes of the pendant groups and the backbones arrangement. Moreover, the different change of the isobaric specific heat with increasing temperature might prove the existence of different thermodynamic states of the samples.

To define an importance of a morphology on assignment of glass transition the disubstituted polynorbornene derivative with shorter spacer was studied too. The higher T_g value of CK(6) was expected owing to the different length of the side chain [9–12, 13]. However, CK(6)I and CK(6)II samples exhibited some endothermal peak in the range of the glass transition, when they were studied as early as 24 h from preparation, see Fig. 1b. The quenching processes for CK(6) and CK(11) derivatives was mainly performed from isotropic state to room temperature. However, one could observe the differences of the DSC curves when samples were quenched from other temperature. This effect occurred particularly strongly with CK(6) samples.

Three experiments were performed in which the quenching was done from 160, 130 and 110°C. It is clear why the data connected with the isotropisation differ and these experiments additionally show that the behaviour of chains being in amorphous regions (the glass transition, Table 2) is strongly affected by LC structure. When the polymer is quenched from different temperatures the different pattern is frozen. Of course, it does not mean that the thermodynamic state obtained in this way is stable. It disappears very often due to relaxation processes, which occur even below T_g, and then new pattern (state) is created.

Table 2 Thermodynamic data of CK(6) samples of different thermal history taken from first heating run

Samples	$T_g(1)$/ °C	$\Delta C_p(T_g)$/ kJ (mol °C)$^{-1}$	$T_g(2)$/ °C	$\Delta C_p(T_g)$/ kJ (mol °C)$^{-1}$	T_t/ °C	ΔH_t/ kJ mol^{-1}	T_i/ °C	ΔH_i/ kJ mol^{-1}
CK(6)I$_{160}$	39.0	0.104	57.9	0.112	126.4	0.07	147.8	2.29
CK(6)I$_{130}$	44.6	0.145	–	–	126.2	0.10	148.3	2.48
CK(6)I$_{110}$	43.8	0.081	54.1	0.066	126.0	0.20	148.3	2.29
CK(6)I$_{rt}$	endo	peak	endo	peak	126.0	0.10	147.3	2.37
CK(6)II	45.7	0.186	–	–	125.8	0.17	147.6	2.52
CK(6)II$_{rt}$	endo	peak	endo	peak	125.8	0.19	147.9	2.24

CK(6)I$_{160,130,110}$ – sample quenched from 160, 130, 110°C;
CK(6)I$_{rt}$ – sample kept at room temperature over 24 h;
CK(6)II – sample cooling down very slowly in step regime

The experiments gave evidences of existing two second-order phase transitions. The values for them were pointed out in the cases when the different heating rates were applied and the values extrapolated to 0°C min^{-1} heating rate were found. The same analysis was done for the endothermal peaks. The glass transition temperatures are 18, 39 and 28, 42°C for CK(11) and CK(6) samples respectively. The isotropisation transition temperatures taken as the maximum point for each endothermal peak are 142 and 143°C. In the case of the derivatives with the shorter spacer another peak fully reproducible was observed and the extrapolated value was found to be 123°C (Figs 2a and 2b).

The concept of some crystal domains existing within amorphous matrix is very often useful for describing of semicrystal polymer properties. It seems to be plausible to apply this concept to LC structure of polymer pattern, and especially for SCLC one, where ordered layers are separated by amorphous regions. In our cases this effect concerning LC domains within amorphous pattern occurs because the tendency of the main chain to adopt its preferred conformation is antagonistic to the mesogenicity of the pendant side groups. This is more evident for the polynorbornene derivatives with the shorter spacer. Most likely, the rather flexible spacer (methylene groups) between the mesogenic group and the main chain is not sufficient to decouple the mobility of the main chain from that of the mesogenic group and the influence of a backbone chain structure on a behaviour of that moiety and vice versa is still significant. In our opinion the influence decreases with the increase of the spacer length. This results in the change of the glass transition temperature as a function of the number of methylene groups [10–12, 14]. Moreover, the dependencies mentioned above could be approximated with two curves intersecting themselves at one point, Fig. 3. This point gives the number of unit required to partially or fully decouple of the backbone from the mesogenic groups. Of course, the intersection point (thereby the spacer length) corresponding to the decoupling effect would be dependent on the backbone configuration formed during polymerisation. It is very important whether *trans* or *cis* isomers are taken into account because of their different stereoregularity [15]. Therefore, one can observe the different values for monosubstituted and disubstituted polynorbornene derivatives. However, the dependencies concerning the polynorbornene derivatives published earlier showed the same tendency [10–12, 14].

The curves concerned with cyanobiphenyl mesogenic group fitted to the open symbols are convergent to T_g value obtained for unsubstituted polynorbornene and this value could be reached when the number of methylene units into side

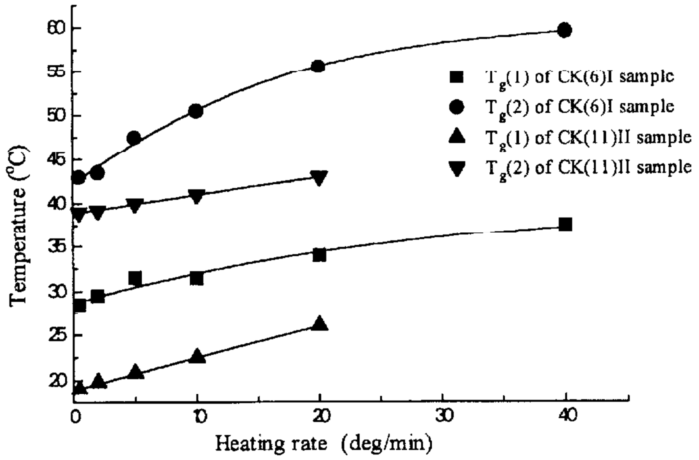

Fig. 2a Extrapolation of glass transition temperatures (T_g) to zero heating rate for selected samples (as indicated in the figure)

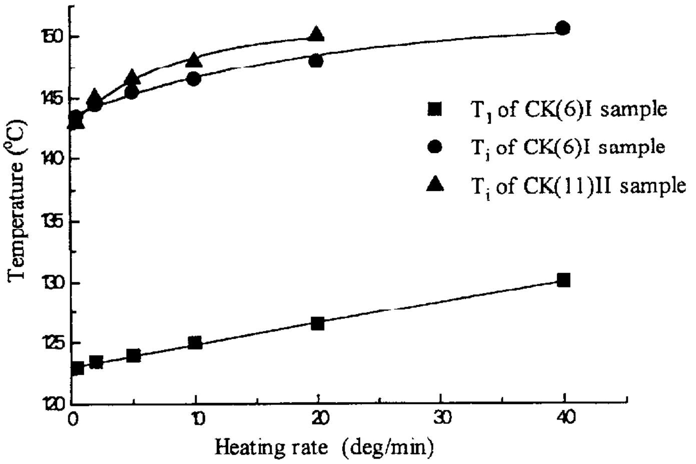

Fig. 2b Extrapolation of isotropisation temperatures (T_i) and of a second transition (T_l) found only for CK(6), details see text

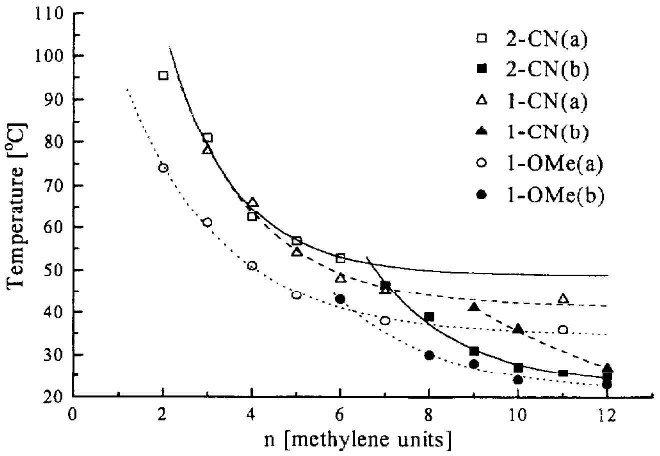

Fig. 3 The fitting procedure of glass transition temperatures of polynorbornene derivatives with different tails *vs.* methylene units. 2-CN means disubstitution of polynorbornene main-chain with cyanobiphenyl groups as mesogens (data points taken from Ref. [12]); 1-CN and 1-OMe mean monosubstitution of backbone with cyanobiphenyl and oxymethyl groups, respectively [9–11]. (a) refers to the main-chain transition and (b) to the side-chain transition of the polymers

chain is rather high. It describes the behaviour of the amorphous regions connecting with the three dimensional backbone rearrangement disturbed by the mesogens with the attached tails, simultaneously treating the methylene groups as a low weight molecular plasticizer. Most likely, the tendency of the mesogenic groups to form the LC structure is stronger than the tendency of the backbone to adopt its preferred conformation, especially when the sample is quenched and the backbones are very disturbed inducing a higher fluidity of the pendant groups.

Monosubstituted derivative with oxymethyl tail show the curve, which most likely due to weaker electrostatic interaction, is a little shifted to lower temperature. When the intersection point of the two curves is approached the polymer pattern behaves as if to be formed with two separate system showing their own glass transition. Therefore, the curve fitted to the solid symbols is interpreted to be the glass transition of the amorphous region created by the side chains. Because, it is the most disturbed region, the effect in DSC traces would be the biggest and it increases with the mass amount of the spacer. In our cases that state is not thermodynamically stable. Therefore, only one glass transition was observed earlier. Nevertheless, our experiments showed two transitions which might result in the shape of T_g *vs.* n found by other authors [10–12]. There are many reasons which might have an influence on this behaviour. First of all, the rigidity of the backbone seems to play a dominate role. In consequence, its configuration must affect on the creation of the LC structure. The attaching second pendant group, with chemically identical formula, to the polymer repeating unit caused the change in stereoregularity which results in the different LC structure compared with monosubstituted derivatives due to the mesogenic group density increasing. In spite of the different LC structure observed in those samples, the dependencies of T_g *vs.* n are similar. Of course, the intersection point for each derivatives has different value but the tendency is still preserved. In the case of SCLC polymer with flexible backbone, e.g. acrylic or methacrylic, the influence of the backbone configuration should be weaker and only one glass transition would occur. The similar chemical structure of the main and the side chain would additionally result in that phase behaviour giving one average T_g value.

Conclusions

SCLC polymers, such as polynorbornene derivatives, may in fact contain three distinct domains: biaxial oriented LC structure, constrained amorphous and unconstrained amorphous which have a major effect on their thermal characteristic, particularly on T_g. The glass transitions for the different samples demonstrate the importance of the morphology on the assignment of the glass transition event. The quenched samples do not show only the change of T_g values but also the drastic changes of the DSC curves giving some evidence of another one glass transition. When the samples were quenched from different temperatures the different pattern were frozen showing that the rather flexible spacer is not sufficient for decoupling of the mobility of the main chain, in our case rather rigid, from that of the mesogenic groups. It is more evident for the polynorbornene derivatives with the shorter spacer that the tendency of the backbone to adopt its preferred conformation is antagonistic to the mesogenicity of the pendant groups.

The different degree of orientation into LC layers (different kind of LC structure) results in varying increases for the glass transition event. The DSC curves show only in some cases the classic step-wise change in T_g indicating that the amorphous domains are constrained and highly restricted in the movement due to the morphology developed as a results of the internal biaxial stretching. It is possible to approximate the experimental data concerning the dependence of T_g *vs.* number of methylene units into spacer with two curves intersecting themselves at one point. The point gives the number of CH_2 units required to partially decouple of the backbone from the mesogenic groups, which resulted in smectic phase creation when the amount of the mesogens per polymer unit is doubling.

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