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Thermal transitions in poly (*N*-alkyl-3,6-carbazolylene)s

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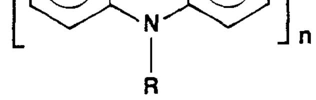
Summary

Thermal transitions of poly (*N*-alkyl-3,6-carbazolylene)s were analyzed by differential scanning calorimetry. Glass transition temperatures (Tg) of the polymers were found to decrease by increasing side-chain length. As-prepared polymers bearing n-octyl pending groups exhibit crystallinity but no crystallisation from the melt was observed. Recrystallisation of the samples thermally treated was obtained by solvent treatment. Crystallinity was associated to an ordered phase involving the main-chain units.

Introduction

Owing to the stiffness of their backbone, many conducting polymers are not processable by solvent or melt techniques. Solutions to these problems have been found in a few cases by attaching aliphatic side-chains to the monomer units of the polymer.This concept has been successfully applied to alkylated polythiophenes (1-3), polyphenylenes (4), polypyrroles(5). Concerning polycarbazolylenes, we recently obtained soluble materials by polymerizing 3,6 dibromocarbazole *N*-substituted by alkyl groups with various chain lengthes (6). Solubility of these polymers allowed on the one hand the determination of their macromolecular and structural features (7) and on the other hand the preparation of solution-cast films (6). Spectroelectrochemical studies of these films have revealed a reversible electrochromism in the oxidation domain, which has been associated with the formation of radical-cations and dications involving carbazolic diads (8). Electrochemical behavior of the deposits has been found to be slightly dependent on the length of the alkyl side-chains.

The present work is devoted to the analysis of the thermal transitions of these poly(*N* -alkyl-3,6-carbazolylene)s together with the study of the evolution of thermal responses as a fonction of alkyl chain length.



poly(*N*-alkyl-3,6-carbazolylene)s
(named PACs)

R = linear alkyl groups : ethyl (PEC) ; n-butyl (PBUC) ; n-octyl (POC) ; n-dodecyl (PDOC) ; n-octadecyl (PODEC).

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Experimental

The different monomers i.e. 3,6-dibromo-*N*-alkylcarbazoles were synthesized according to the method previously described for the *N* -ethyl derivative (9). These compounds were characterized by ^{1}H and ^{13}C NMR and by elemental analysis (purity > 99.5 %).

PACs were electrosynthesized according to the procedure described for PEC (9) involving the cathodic reduction of the $NiBr_2$ / 2,2' bipyridine / 3,6-dibromo-*N*-alkylcarbazole system in *N,N* dimethylacetamide. The overall reaction scheme is the following :

$$n\ \text{Br-Ar-Br} + 2\,n\,e^- \xrightarrow{\text{Ni (O)}} \text{-(Ar)}_n\text{ -} + 2n\ \text{Br}^-$$

with Ar = *N*-alkyl-3,6-carbazolylene

After work-up PACs were soluble in organic solvents such as THF and $CHCl_3$ and were characterized by ^{13}C NMR (10) and by size exclusion chromatography in THF using a Waters GPC apparatus calibrated with standard polystyrenes.Depending on the preparation conditions the PACs samples had molar mass distributions from multimodal (case of the low molar mass samples) to monomodal (higher molar mass samples) with $\overline{M}n$ ranging from 1300 to 8600 g.mole^{-1} and a polydispersity $1.2 \leqslant \overline{M}w / \overline{M}n \leqslant 2.1$ (Table 1).

Differential scanning calorimetry analyses were performed with a Perkin-Elmer DSC-4 apparatus calibrated with indium (T_m =156.6 °C and ΔHm = 28.4 J.g^{-1}). Glass transition temperatures (Tg) were recorded at the half height of the corresponding heat capacity jump, and the temperatures of melting (Tm) were determined at the maximum of the endotherm. A heating rate of 10°C.min^{-1} was used in all cases.

X-ray diffraction profiles of POCs samples in powder form were obtained using a Rigaku Rotaflex RU-200 BH diffractometer with a rotating anode, operating at 55kV and 190mA and with a nickel-filtered Cu Kα radiation (λ = 0.1542 nm).

Results and discussion

As shown in Table 1, PACs exhibit a glass transition which gradually decreases from 180°C to - 32°C by increasing side-chain length from ethyl to octadecyl respectively. A similar variation of Tg with the length of the pending group has been already described for comb-like structured polymers such as e.g. poly(n-alkylmethacrylate)s (11) and recently for conducting polymers as poly(3-alkylthiophene)s (12). This is consistent with the general concept that with increasing side-chain length, transition properties change from a typical polymeric behavior to that of a smaller molecule with side-chain features more marked (13).Furthermore from the results obtained for PBUCs and POCs (see Table 1) it may be observed that for a given alkyl chain length Tg increases with $\overline{DP}_n$.

It is noteworthy that for POCs , thermograms of the first scan exhibit an endothermic transition (Figure 1). The energy and temperature of this transition depend on $\overline{DP}_n$. For POC_1 ($\overline{DP}_n$ = 7), the transition occurs between 110°C and 145°C with a maximum of the endotherm at Tm = 132°C and an enthalpy of 1.71 kJ. mole^{-1} (ΔH per mole of repeat unit). For POC_2 ($\overline{DP}_n$ = 31), it appears between 125°C and 162°C with Tm = 153°C and ΔH = 4.34 kJ. mole^{-1}. We shall focus the discussion on this transition.

Polymer	$\bar{M}_n$. 10^{-3}	$\bar{M}_w$. 10^{-3}	$\bar{M}_w / \bar{M}_n$	T_g (°C)	T_m (°C)	ΔH (kJ.mole^{-1})
PEC	1.0	2.1	2.1	180	----	----
PBUC1	1.9	3.6	1.9	180	----	----
PBUC2	3.3	4.9	1.5	215	----	----
POC1	1.9	2.9	1.5	60 ^{a}	132 ^{a}	1.71
				70 ^{b}	----	----
POC2	8.6	10.0	1.2	70 ^{a}	153 ^{a}	4.34
				113 ^{b}	----	----
PDOC	3.7	5.2	1.4	15 ^{a}	60 ^{a}	0.49 ^{c}
				15 ^{b}	----	----
PODEC	1.8	3.4	1.9	-32	----	----

Table 1 : Macromolecular and thermal features of PAC samples.
a: first heating scan ; b: second an subsequent scans
c: weak signal.

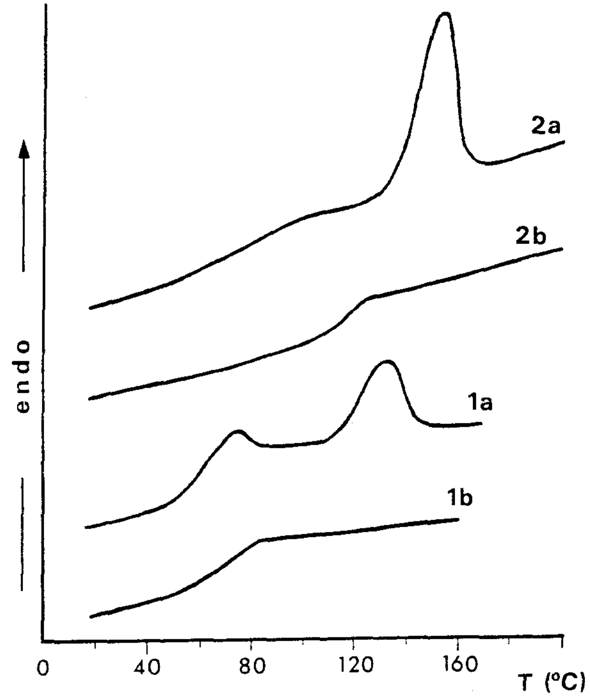

Figure 1 : DSC thermograms of POCs. 1: POC$_1$. 2 : POC$_2$.
a: first scan. b: second and subsequent scans.

The endotherm can be attributed to the melting of a crystalline phase. Indeed, X-ray analysis reveals the presence of diffraction peaks for POC$_1$ and POC$_2$ (Fig. 2). The intensity of the peaks is higher for POC$_2$ than for POC$_1$.This is in agreement with the larger value of ΔH for POC$_2$ than for POC$_1$. Furthermore, diffraction peaks disappear after a thermal treatment of the sample at 175°C for ten minutes (Fig. 3). The remaining signal is a broad peak characteristic of the amorphous state. In comb-like structured polymers, examples have been reported where a crystalline organization involving only the alkyl side-chains is observed providing that the number of carbon atoms is higher than 9-12 (13,14).In these cases melting temperatures are lower than 80°C (14).In some cases, a second endotherm attributable to the melting of an ordered phase involving either the sole main chain (12) or both the main chain and the alkyl side-chains (15) is observed . For POCs, the shortness of the alkyl side-chains and the high temperature of melting (Tm =132°C for POC$_1$ and 153°C for POC$_2$), support the attribution of the endotherm to the melting of an ordered phase involving the main chains and possibly the alkyl side-chains.

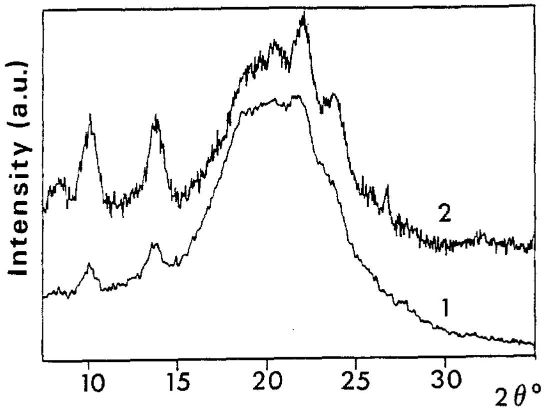

Figure 2 : X-ray diagram of as-prepared POCs powders;
1: POC$_1$ ($\overline{DP}_n = 7$)
2: POC$_2$ ($\overline{DP}_n = 31$)

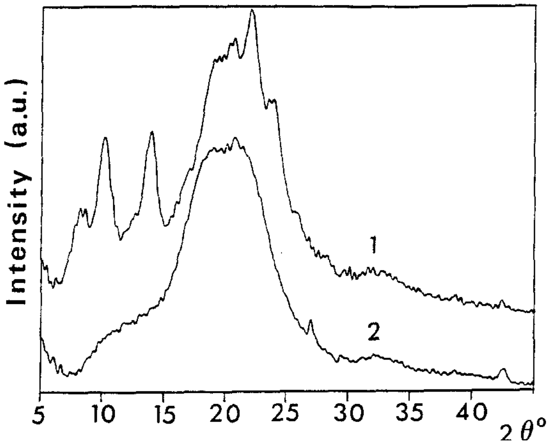

Figure 3 : X-ray diagram of POC$_2$.
1: original sample.
2: after thermal treatment at 175°C during ten minutes.

The transition is thermally irreversible since no exotherm was observed either on cooling or on the subsequent heating runs, even after annealing for 88 hours at various temperatures.Nevertheless, the initial behavior of POC_2 can be reobserved after redissolution and reprecipitation of the sample thermally treated.This work-up restore the same thermal features as those observed on the first run and in particular gives rise to the same enthalpy and Tm values. Some insights on this behavior can be obtained from the variation of the glass transition temperature with thermal treatment. On the first scan , the values of T_g are 60°C for POC_1 and 70°C for POC_2 and raise to 70°C and 113°C respectively on the second and subsequent scans. This in contrast to the behavior of semi-crystalline polymers for which the glass transition temperature is either independent of crystallinity or higher for the semi-crystalline sample than for the totally amorphous one. These results indicate that for POCs, melting leads to an amorphous state different from the initial one co-existing with the crystalline phase.It may be reminded that the initial semi-crystalline samples were obtained from a work-up of the materials (dissolution-precipitation).Solubilization in common solvents of such comb-like polymers with a rigid backbone, is mainly induced by the solubility of the alkyl side-chains.Hence, one can expect that the crystallisation occuring during the precipitation is governed by the ordering of the aromatic backbone.Thus, the ratio of the number of flexible alkyl side-chains to the number of rigid backbone units involved in the amorphous phase is higher in the semi-crystalline sample resulting from the dissolution-precipitation process than in the totally amorphous one obtained on cooling from the melt.Consequently, a higher Tg is observed for the latter than for the former in which the crystalline phase would be, then, composed of main-chain units only.

The increase of Tg resulting from the first heating run leads to a decrease of the range of temperature Tm-Tg in which crystallisation of the supercooled liquid could take place. Hence, bulk crystallisation is kinetically hindered owing to the impossibility to find a range of temperature between Tm and Tg for which the degree of supercooling is large enough and the viscosity sufficiently low. Of course, this effect holds mainly for POC_2. For POC_1, one must take into account the low molar mass and multimodal distribution and consequently chain-end effects on the value of Tg and on the ability to crystallise.

PACs exhibit some features similar to poly(3-alkylthiophene)s (P3ATs) as already cited (12). P3ATs exhibit crystallinity. For P3ATs with alkyl groups longer than butyl, the more generally accepted ordering of the crystalline phase is a planar alternating zigzag conformation of the thiophene units along the polymer backbone, separated by ordered or disordered alkyl side-chains (12,15). For POCs,though no structural analysis from X-ray diffraction profiles has been conducted, some insights have been obtained using molecular models. If the alkyl side-chains of adjacent carbazole units are in a syn position, a torsion angle between these units is required to minimize steric interactions. Hence, a helical conformation results.Successive alkyl groups in an anti position allow coplanarity of the corresponding carbazole units and consequently a lamellar structural organization similar to P3ATs may be obtained.

Finally, among the PACs studied, POCs were the only materials for which an endothermic transition clearly appeared, though a small signal (ΔH =0.49 $kJ.mole^{-1}$ and Tm = 60°C) was observed in the case of PDOC. It may be concluded that for the PACs studied, eight carbon atoms in the n-alkyl side chain is the optimum length allowing the formation of a crystalline organization induced by favorable polymer-solvent interactions.

Conclusion

Calorimetric measurements of poly (*N*-alkyl-3,6-carbazolylene)s revealed that Tg gradually decreases by increasing the length of the alkyl group from ethyl to octadecyl. Among the PACs studied, only POCs exhibit crystallinity. No crystallisation from the melt was observed. Nevertheless, the thermal features of POCs thermally treated were completely restored by solvent treatment. Crystallinity was attributed to an ordered phase involving the main chains only.

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