

*Dedicated to Prof. Antonius Kettrup on the occasion of his 60th birthday*

## **A DSC-STUDY OF DONOR/ACCEPTOR SIDE-CHAIN POLYMERS WITH FLUORINATED TAPER-SHAPED TAILS**

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### **Abstract**

It is shown that insertion in methacrylic polymers of bulky electron donor/acceptor side-groups with taper-shaped fluorinated tails promotes a self-organization of the respective side-chain polymers due to the space demands of the bulky D/A side-groups, leading to a columnar hexagonal mesophase. The presence of an Lc-phase is evidenced by DSC and identified by X-ray analysis. The orientation in the respective copolymers and polymer blends is additionally improved by the CT-interaction between the D/A side-groups. An increased packing effect due to this CT-orientation effect is evidenced in DSC by an increase of the respective transition temperatures. CT-interaction is responsible as well for a preferential polymerization of monomeric D/A-complexes leading to copolymers of alternating structures and for a "zip"-like arrangement along the main chain of the A/D-complexes between the interacting side-groups in polymer blends. Formation of mesophases is even observed in CT-interacting blends between the Lc-D/A side-chain polymethacrylates and the respective amorphous D/A side-chain polysiloxanes.

**Keywords:** amorphous D/A side-chain polysiloxanes, copolymers and blends, DSC-study of D/A polymeric systems, Lc-D/A side-chain polymethacrylates, self-organization and CT-interaction

### **Introduction**

Proceeding from the observation that side-chain crystallization of amorphous polymers containing donor carbazolyl side-groups can be induced by charge transfer interaction with a low molecular crystalline bisacceptor [1], we have demonstrated in a second paper [2] the possibility to realize by self-organization mesophasic structures in polymeric systems due to the interplay between CT-complexation of the carbazolic donor group and the fluorophobic effect of the tapered tails of donor main-chain poly-(3,6-carbazolylmethylene)s. It has also been shown that mesophases can be induced in amorphous donor carbazolylic

copolymers bearing both donor groups with fluorinated and aliphatic tapered tails. The condition is, however, that only the fluorinated donor sites of the copolymer are selectively complexed with a corresponding low molecular fluorinated acceptor. The CT-complexation effect alone is not strong enough to overcome the fluorophobic effect of the donor sites if instead of the fluorinated acceptor an aliphatic low molecular acceptor is used for complexation of the donor sites with tapered aliphatic tails of the copolymer.

In the present paper we report on mesophase formation in donor/acceptor methacrylic polymers bearing bulky side-chain donor/acceptor interacting groups with fluorinated tails. Mesophase formation is explained by the space demands of the bulky side-groups. In copolymers and blends of the D/A side-chain methacrylates the mesophases are additionally stabilized by a "zip"-like arrangement of the CT-complexes along the main chain. Mesophase formation is also observed in blends between these Lc-D/A side-chain methacrylic polymers and the corresponding amorphous D/A side-chain polymethylsiloxanes.

## Experimental

The D/A side-chain polymers used in this study were synthesized in our laboratories by adapting partly synthetic routes recommended in literature, but developing also new ways for obtaining finally the Lc-D/A side-chain methacrylic polymers bearing fluorinated tails next to the interacting side-groups. Details concerning the synthesis of the monomers will be described elsewhere. An overall simplified reaction scheme is presented in Fig. 1.

After protection with diphenylmethane (2) [3] of two of the phenolic groups of the methylic ether of gallic acid (1), the remaining phenolic group of the intermediate (3) was esterified with bromo-undecane-1-ol (4). Subsequently the protective group of intermediate (5) has been removed [4] and the two recovered phenolic groups of (6) were substituted by heptafluorododecane-1-yloxy – groups (7). Then the methylic ester group of the resulted compound (8) was replaced [5] by either the acceptor 3,5-dinitrobenzoyl-ethoxy-ethyl – (10a) or by the donor 2-carbazolyl-ethoxy-ethyl – group (10d). Next the undecanolic group of (11a, 11d) was esterified according to literature, using methacrylic acid chloride in presence of pyridine [6] resulting finally the methacrylic acceptor – M-A- respective donor – M-D- monomers, i.e. 2-(2-(3,5-dinitrobenzoyloxy)-ethoxy)ethyl-3(*n*...) and 2-(2-(carbazolyl)ethoxy)ethyl-3(*n*-11-methacryloxyundecane-1-yloxy)-4,5-di(*n*-5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12,heptafluorododecane-1-yloxy)-benzoate, respectively. Improved yields and purer D/A- monomers were obtained, however, if the pyridine was substituted by molecular sieves suspended in CCl<sub>4</sub> and the mixture was refluxed for 12 h at the boiling temperature of CCl<sub>4</sub>.

The monomers were subsequently dissolved in toluene and polymerized at 60°C in the presence of AIBN. Polymerization of the donor monomer by 'atomic

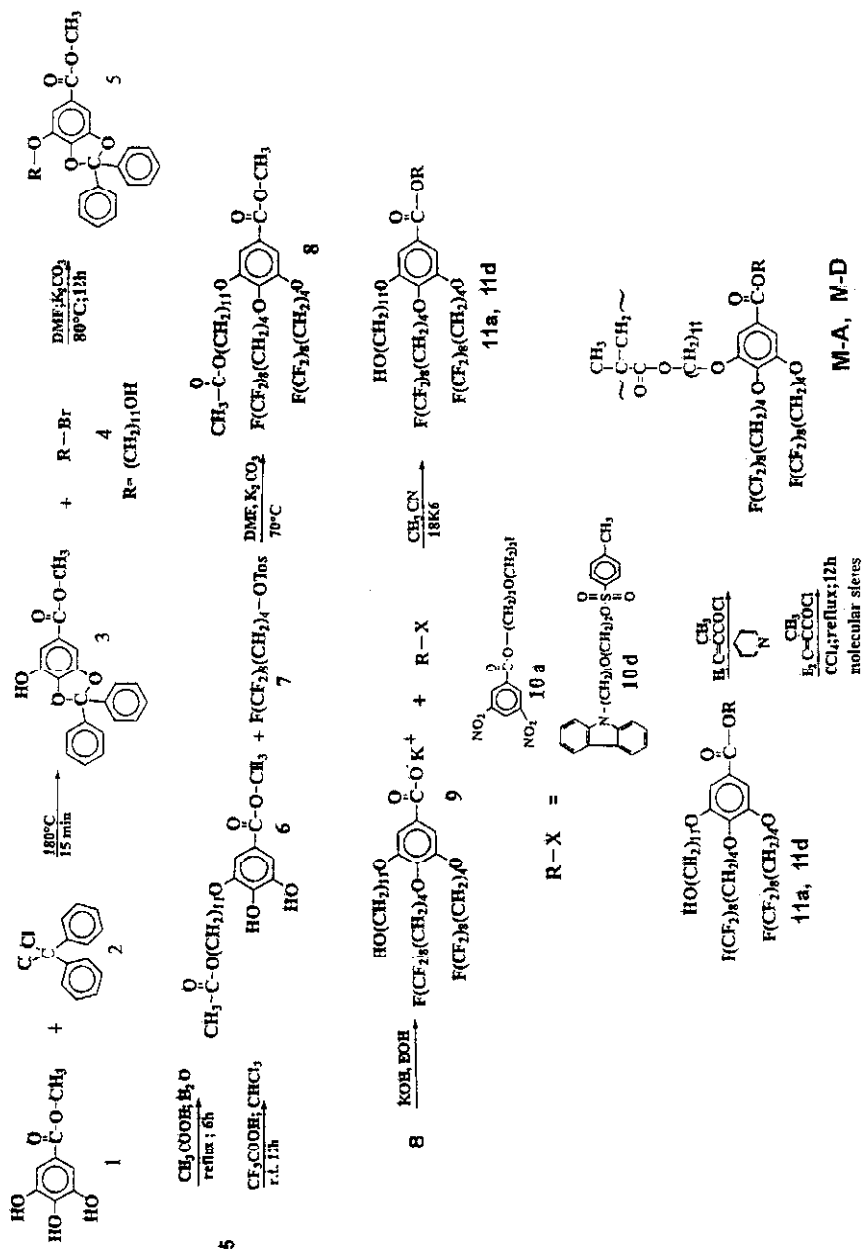


Fig. 1 Reaction scheme of the synthesis of the donor/acceptor *Le* side-chain methacrylic monomers with tapered-shaped fluorinated tails, M-A and M-D

transfer polymerization' [7] resulted, however, in a polymer with improved properties.

All intermediates and both the monomers and polymers were characterized by elemental analysis,  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  and  $^{19}\text{F-NMR}$ . Additionally the polymers were characterized by GPC in toluene at  $80^\circ\text{C}$  using PS standards and by DSC. The DSC-traces evidenced the presence of a mesophase and by X-ray analysis it was confirmed that both monomers and polymers present a columnar hexagonal mesophase.

Beside the methacrylic Lc-D/A side-chain polymers with fluorinated tails were used for CT-complexation also amorphous D/A side-chain polymethylsiloxanes without fluorinated substituents, but bearing the same carbazolyl donor- and 3,5-dinitro-benzoyl acceptor groups, respectively. They were obtained by hydrosilylation of a commercial polymethylhydrosiloxane in the presence of a  $\text{Pt}^{(0)}$  catalyst. The structures of the amorphous D/A side-chain polysiloxanes, i.e. of the acceptor poly[(3-(3,5-dinitrobenzoyloxy)propyl)methylsilicone] –

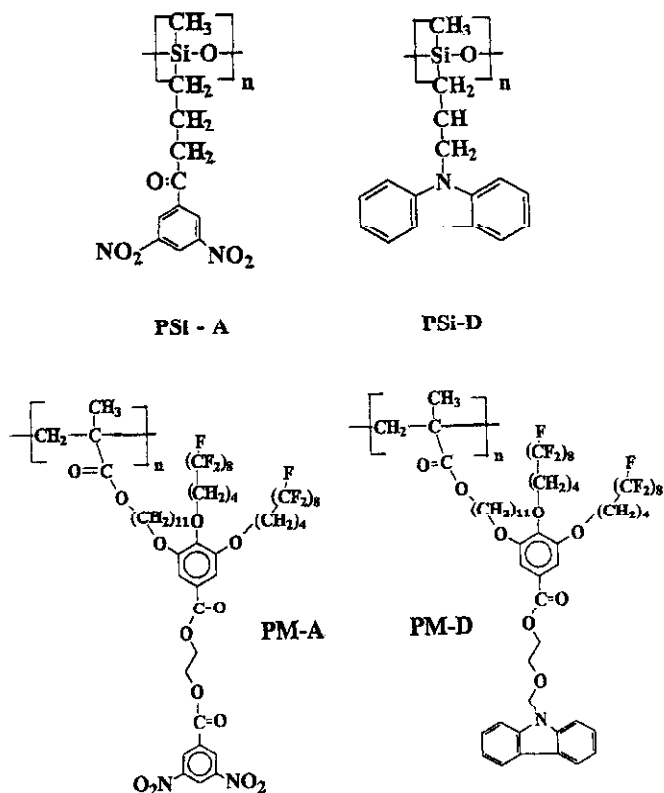


Fig. 2 Structures of the repeating units of the donor/acceptor side-chain amorphous polysiloxanes, PSi-A and PSi-D, and Lc polymethacrylates, PM-A and PM-D

**Table 1** Molecular characteristics and transition temperatures of D/A side-chain polymers

| Polymer | $M_n$              | $M_w/M_n$ | $T_g/^\circ\text{C}$ | $^aT_{\phi}/^\circ\text{C}$ | $^bT_{\text{iso}}/^\circ\text{C}$ |
|---------|--------------------|-----------|----------------------|-----------------------------|-----------------------------------|
| PSi-A   | 2720               | 1.3       | 19.2                 | –                           | –                                 |
| PSi-D   | 2700               | 1.7       | 54.0                 | –                           | –                                 |
| PM-A    | 27000 <sup>c</sup> | trimodale | 8.1                  | 74.2                        | 72.4                              |
| PM-D    | 21000 <sup>d</sup> | trimodale | 11.4                 | 86.2                        | 79.2                              |

<sup>a</sup> $T_{\phi}$  – temperature of isotropization evidenced in second heating scan, h.r. = 10 K min<sup>-1</sup>

<sup>b</sup> $T_{\phi}$  – temperature of mesophase forming evidenced in first cooling scan, c.r. = -10 K min<sup>-1</sup>

<sup>c</sup> main fractions: 21000 – 51%, 3400 – 18%

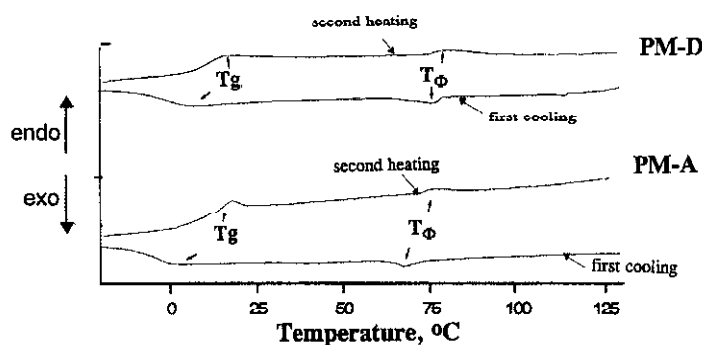
<sup>d</sup> main fractions: 27000 – 35%, 3550 – 53%

PSi-A- and of the donor poly[(3-carbazolyl-propyl)methylsilicone] – PSi-D – together with those of the corresponding Lc-D/A side-chain polymethacrylates are shown in Fig. 2.

The main characteristics of the side-chain D/A polymers employed for the subsequent CT-complexation studies by DSC, using a Perkin-Elmer DSC7 with heating and cooling rates of 10 K min<sup>-1</sup>, respectively, are presented in Table 1.

## Results and discussion

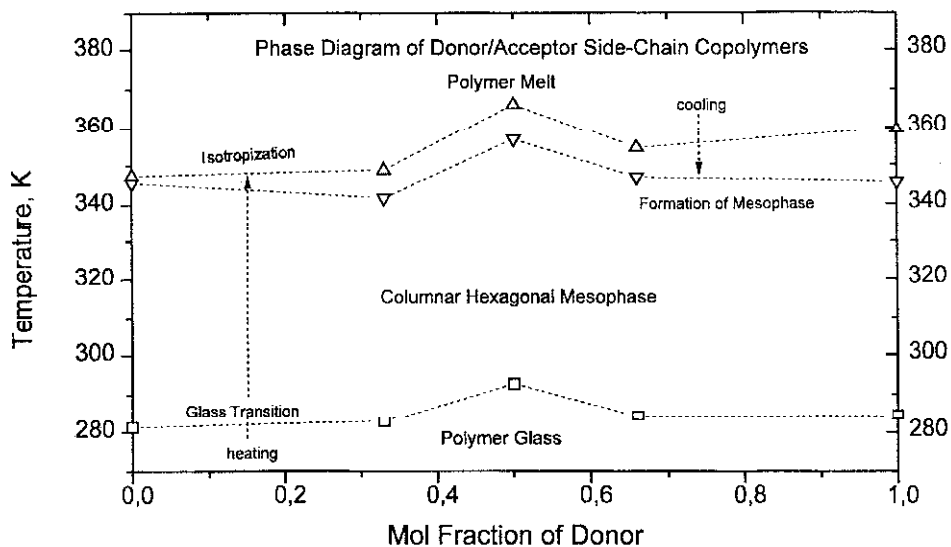
Typical DSC-scans obtained at heating and cooling rates of 10 K min<sup>-1</sup>, respectively, for the methacrylic side-chain D/A polymers PM-A and PM-D with interacting D/A side-groups bearing fluorinated tails are presented in Fig. 3. The presence of an additional phase between the polymeric glass and the polymeric melt, delimited by the glass temperature,  $T_g$ , and the temperature of isotropization,  $T_{\phi}$ , is evident in both the first cooling and the second heating scans. The low



**Fig. 3** DSC heating and cooling scans of the Lc-D/A side-chain polymethacrylates  $T_g$  – glass temperature,  $T_{\phi}$  – temperature of transition between Lc-mesophase and isotropic melt (heating – isotropization; cooling – mesophase forming) (first cooling and second heating scans – rates 10 K min<sup>-1</sup>)

values of the transition enthalpies ( $0.273 \text{ kcal mol}^{-1}$  for PM-A respective  $0.304 \text{ kcal mol}^{-1}$  for PM-D) suggested the presence of a mesophase and by X-ray studies has been evidenced the existence of a columnar hexagonal mesophase, which is explained by the space demands of the bulky interacting D/A side-groups with fluorinated tails. Molecular modeling attempts support this supposition.

For the beginning it has then been proved if intramolecular CT-complexation within copolymers containing both the acceptor M-A and donor M-D repeating units with interacting side-groups bearing fluorinated tails, respectively, perturbs the development of a columnar hexagonal mesophase observed for the homopolymers. Three D/A copolymers were synthesized with the A/D ratio of respective 2:1 (Copoly- $A_2D$ ), 1:1 (Copoly-AD) and 1:2 (Copoly- $AD_2$ ). Corresponding DSC studies exhibited traces very similar to those of the homopolymers shown in Fig. 3 and in Fig. 4 is presented the phase diagram of these Lc-donor/acceptor side-chain methacrylic copolymers. All copolymers showed the presence of the mesophase but the respective transition temperatures were increased compared to the values estimated accordingly to additivity rules. The largest positive deviations from additivity show the transition temperatures of 1:1 Copoly-AD and simultaneous studies of copolymerization kinetics suggested an increased tendency for alternating structures due to a preferential polymerization of the 1:1 D/A monomer complexes. D/A complexation will be ac-



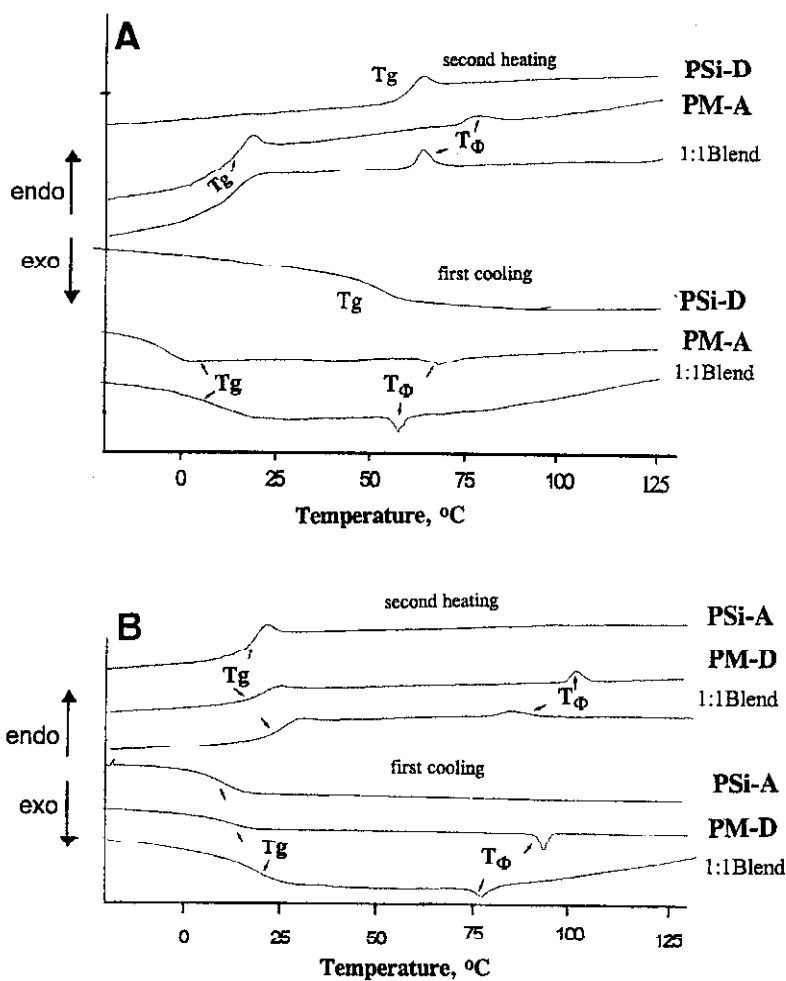
**Fig. 4** Phase diagram of the Lc-D/A side-chain methacrylic polymer system. Squares – glass transition temperatures, Triangles: upwards – temperatures of isotropization during heating; downwards – temperatures of mesophase forming during cooling

accompanied, however, by a closer packing of the repeating units i.e. by a reduction of the free volume and of the appropriate conformational entropy and thus by an equivalent increase of the respective transition temperatures. As the probability of the monomeric D/A-complexation is maximum for a stoichiometric ratio of D/A monomeric units, the 1:1 Copoly-AD shows the closest packing and thus the largest deviations from additivity of the respective transition temperatures.

The DSC investigation were subsequently extended in a next step to the study of intermolecular CT-complexation between the interacting donor and acceptor repeating units of the 1:1 blend of the Lc-D/A side-chain polymethacrylates, PM-A and PM-D, respectively. The DSC traces proved once more to be very similar to those of the homopolymers shown in Fig. 3. Again were observed positive deviations from additivity of the respective transition temperatures of the blend indicating the denser packing in the PM-A/PM-D blend than in the blend components. The deviations from additivity were, however, less pronounced as for the 1:1 Copoly-AD, suggesting a looser packing in the blend than in the copolymer. This may be explained by the smaller probability of CT-complexation in the 1:1 A/D blend compared to that of the 1:1 Copoly-AD with prevailing alternating structure due to the preferentially polymerization of monomeric A/D-complexes.

The observed improved packing effect in the 1:1 PM-A/PM-D blend compared to that of its components is explained by an increased CT-complexation probability due to a "zip"-like orientation effect along the polymeric main chains induced by the interacting acceptor and donor side groups. This "zip"-like orientation effect on the main chains promotes the tendency of additional CT-complexation of the interacting side groups. It was assumed for the first time to explain the experimentally observed improved CT-complexation probability in flexible D/A polysiloxane blends compared to that of the stiffer D/A polymethacrylate blends [8]. The favourable influence of the increasing spacer length between the interacting groups and the polymeric backbone on the positive deviation from additivity of the glass transition temperatures of amorphous electron-donor/electron-acceptor polymethacrylic blends was also attributed to this "zip"-like orientation effect of the CT-interaction within D/A blends [9].

Finally has been investigated the CT-complexation behaviour between the Lc-A/D side-chain polymethacrylates and the corresponding amorphous-A/D side-chain polysiloxanes bearing the same electron-interacting donor and acceptor groups, but without fluorinated tails. In Fig. 5 are exhibited the respective DSC-thermograms. The DSC-traces of the amorphous side-chain donor PSi-D and of the Lc side-chain acceptor PM-A, together with those of their 1:1 A/D blend are compared in Fig. 5a, whereas those of the amorphous PSi-A, the Lc PM-D and the corresponding 1:1 A/D blend are shown in Fig. 5b. It is interesting to notice that both blends of the interacting amorphous side-chain polysiloxanes with the appropriate Lc side-chain polymethacrylates show clearly the presence



**Fig. 5** DSC heating and cooling scans of D/A side-chain amorphous polysiloxanes, Lc polymethacrylates and of their 1:1 blends. A – Donor polysiloxane, PSi-D, and acceptor polymethacrylate, PM-A; B – Acceptor polysiloxane, PSi-A, and donor polymethacrylate, PM-D (for significance of temperatures see Fig. 3)

of a mesophase. But based alone on the shape of DSC-traces and the respective enthalpies of isotropization ( $0.123 \text{ kcal mol}^{-1}$  for PSi-A/PM-D, respective  $0.134 \text{ kcal mol}^{-1}$  for PSi-D/PM-A) it is not possible to decide if the amorphous polysiloxane blend component acts as a plasticizer on the Lc-D/A polymethacrylates or if a new specific mesophase is induced in the amorphous/Lc D/A blend. Taking into account, however, that at least the PSi-D/PM-A blend shows a glass temperature situated well below additivity, sooner a plasticizer effect of the mo-



bile polysiloxane backbone may be supposed. Careful X-ray studies may give an answer.

The respective specific transition temperatures of the Lc-AD side-chain polymethacrylates, PM-A and PM-D, their 1:1 Copoly-AD and 1:1 PM-A/PM-D blend as well of the A/D blends between amorphous D/A side-chain polysiloxanes and Lc side-chain D/A polymethacrylates are compared in Fig. 6.

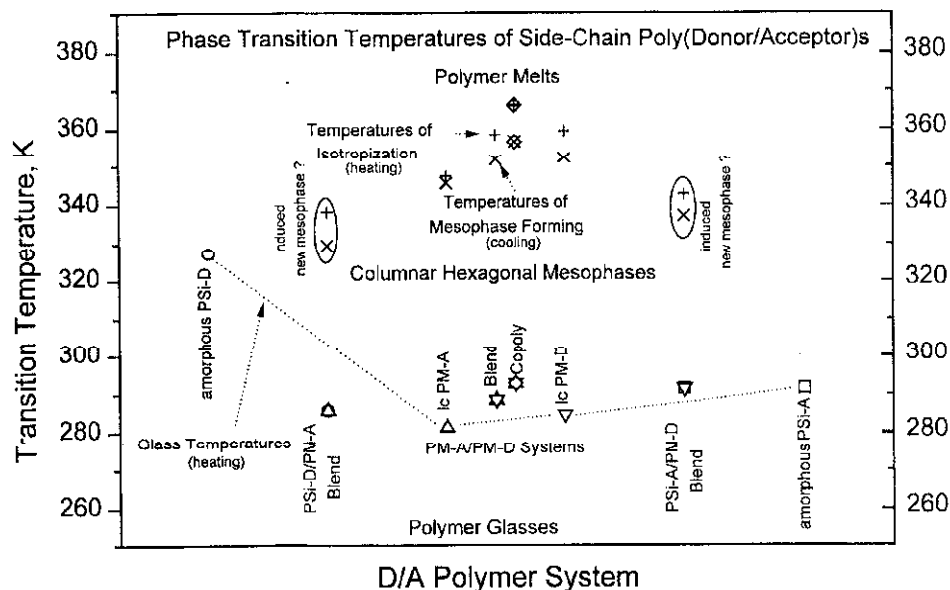


Fig. 6 Comparative diagram of the DSC phase transition temperatures of the studied D/A side-chain polymeric systems

In conclusion it has been shown that the introduction of bulky interacting D/A side-groups with fluorinated taper-shaped tails in methacrylic polymers causes the development of hexagonal columnar mesophases due to self-organization tendencies promoted by the space demand of the fluorinated bulky interacting D/A side-groups. The development of mesophasic structures in copolymers is additionally increased due to the observed tendency for alternating structures because of the preferential polymerization of monomeric D/A-complexes. The development of mesophasic structures in D/A blends, on the other hand, is mainly attributed to a preferential "zip"-like arrangement along the main chains of the complexes of the interacting D/A side-groups of the blend components.

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One of the authors (M.B.) is obliged to Prof. Percec of the Case Western Reserve University, Cleveland, for helpful scientific indications and comments. Financial support of the Deutsche Forschungsgemeinschaft (SFB 60) is gratefully acknowledged.

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