

Influence of flexible oligo(tetraflouroethene) segments on the glass temperature of poly(aramide)s and poly(amide imide)s

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Dedicated to the 65th anniversary of Prof. Dr. Dr.-Ing. E. h. Hansjörg Sinn

Summary

The insertion of oligo(tetraflouroethene) segments into the main chain of poly(aramide)s and poly(amide imide)s is accompanied by a decrease of the glass temperature. The decrease is strictly related to the number of CF_2 -units and is the same for both poly(aramide)s and poly(amide imide)s. The absolute glass temperature depends, however, on the initial structures of the monomeric units. As a consequence 'mastercurves' can be constructed by shifting the individual T_g vs. number of CF_2 -units curves along the temperature axis. A detailed analysis of the data indicates that besides the T_g - mass/'flexible' bond of monomeric unit criterion additional volume and interaction dependant packing effects have to be considered for an accurate prediction of the glass temperatures of polymers.

Introduction

Flourine-containing polymers are characterized by high thermoxidative stability and fire retardancy, environmental and chemical stabilities, low water uptake and low surface energy, as well as by decreased dielectricity and refractive indices. The insertion of flexible oligo(tetraflouroethene) segments into main chain polymers can be accompanied by increased toughness combined with reduced phase transition and processing temperatures without sacrificing other useful properties.

Taking into account the intrinsic high thermal stabilities and good mechanical properties of poly(aramide)s and

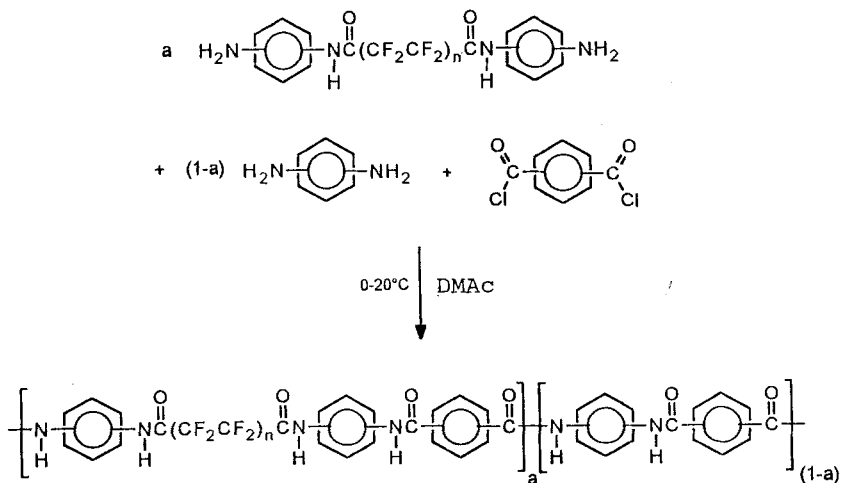
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poly(amide imide)s, it seemed useful to study the effect of insertion of oligo(tetrafluoroethene) segments into the main chain of these polymers. In addition to other properties a decrease of the glass temperature has been observed. The present paper reports some regularities of the glass temperature changes caused by the insertion of tetrafluoroethane-, octafluorobutane- and dodecafluorohexane segments into linear poly(aramide)s and poly(amide imide)s. The syntheses of such fluorine-containing poly(aramide)s⁽¹⁾ and poly(amide imide)s⁽²⁾ are described in detail elsewhere.

The ultimate goal of the study is to present additional hints for the influence of structural parameters on the glass temperature of polymers, taking into account the observed influences of both the spacer length and the attached end group on the glass temperature of poly(methacrylate)s⁽³⁾ and of the insertion of an increasing number of adjacent phenylene thioether units in main chain poly(phenylene ether ketone)s⁽⁴⁾.

Experimental

The **polyaramides** were synthesized by polycondensation reaction of the respective phenylenediamines - which may contain or not oligo(tetrafluoroethene)-segments - with dichlorides of isophthalic and terephthalic acid, respectively. The overall reaction pathway is presented in Scheme I and some characteristics of the polymers of the isophthalic acid (IA-m) obtained in the presence of dimethylacetamide - DMAC - are shown in Table I.



Scheme I. Synthesis of Poly(aramide)s

Using mixtures of phenylenediamines without and with oligo(tetraflouroethene)-units, 'segmented polymers' were obtained. The segmented poly(aramide)s of the terephthalic acid were highly crystalline.

Table I Characteristics of m-Poly(aramide)s with Oligo(tetraflouroethene)-Segments

Structural units										
	a	0,2			0,5			1		
n	-	1	2	3	1	2	3	1	2	3
Polymer	IA-m	IA-4m1	IA-8m1	IA-12m1	IA-4m2	IA-8m2	IA-12m2	IA-4m3	IA-8m3	IA-12m3
Tg, K ^{a)}	545	526	509	503	520	503	494	518	496	486
$\eta_{inh}^{b)}$	1.31	1.29	1.38	1.29	1.26	0.93	1.26	1.05	1.07	1.45

a) by DMA - maximum of tan δ

b) η_{inh} (dl/g) determined in DMF/LiCl(5%)-solution at 30°C

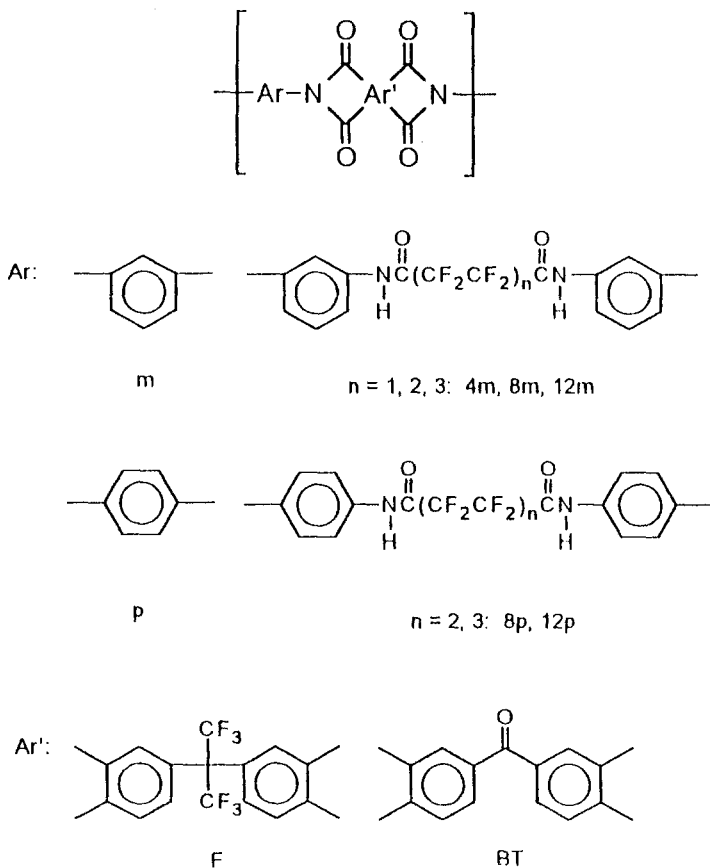
The *poly(amine imide)s* were obtained by polycondensation of aromatic dianhydrides - i.e. 2,2-bis-(3,4-dicarboxyphenyl) hexaflouropropane dianhydride, 6F, and 3,3',4,4'-benzophenone-tetracarboxylic dianhydride, BT - with m- or p-diamines with or without oligo(tetraflouroethene) segments in a two step reaction via the respective poly(amide carboxylic acid)s (see Scheme II and Table II).

Table II Characteristics of Poly(amide imide)s with oligo(tetraflouroethene)-Segments

Polymer	6F-m	6F-4m	6F-8m	6F-12m	6F-p	6F-8p	6F-12p
Tg, K ^{a)}	574	518	505	491	625	558	538
$\eta_{inh}^{b)}$	1.03	0.42	0.70	0.58	0.84	0.83	0.86
Polymer	BT-m		BT-4m		BT-8m		BT-12m
Tg, K ^{a)}	548		505		486		472
$\eta_{inh}^{b)}$	0.43		0.40		0.70		0.73

a) by DMA - maximum of loss modul, E''

b) in (dl/g) determined in DMF at 30°C



Scheme II. Synthesis of Poly(amide imide)s

All polymer structures were verified by elemental analysis using the Perkin-Elmer CH-3600 analyzer, by FT-IR on a Bruker IFS FT-IR Spectrometer and by $^1\text{H-NMR}$ spectroscopy on a Bruker ARX 300 spectrometer at 300 MHz.

The rheological properties of the polymers were determined by dynamic mechanical analysis, DMA, with the Rheometrics Solid Analyser RSA II using compression-molded bars of 60x5x2 mm in the dual-cantilever geometry at a deformation of 0.1% induced with the frequency of 1 Hz. The glass temperature has been attributed to the maximum of $\tan \delta$.

Results and Discussion

The dependence of the glass temperature of the studied fluorine-containing rigid aromatic polymers on the number of flexible CF_2 -groups of the perfluoroalkylene segment inserted into the main chain is illustrated in Fig. 1A. The absolute value of the glass temperature depends unequivocally on the initial structure of the stiff aromatic main chain polymer. The decrease of the glass temperature, on the contrary, seems to be identical for the same number of flexible CF_2 -groups inserted in the same position between the phenylene rings of the diamine group, independent of the original structure of the repeat unit. As a consequence, the individual curves glass temperature vs. number of CF_2 -groups in the monomeric unit can be superposed to a 'mastercurve' as shown in Fig. 1B.

Moreover it results that the glass temperatures of para-6F polymers are higher with respect to those of meta-6F polymers, suggesting a smaller 'free volume', i.e. a closer packing due to the symmetrical para structure.

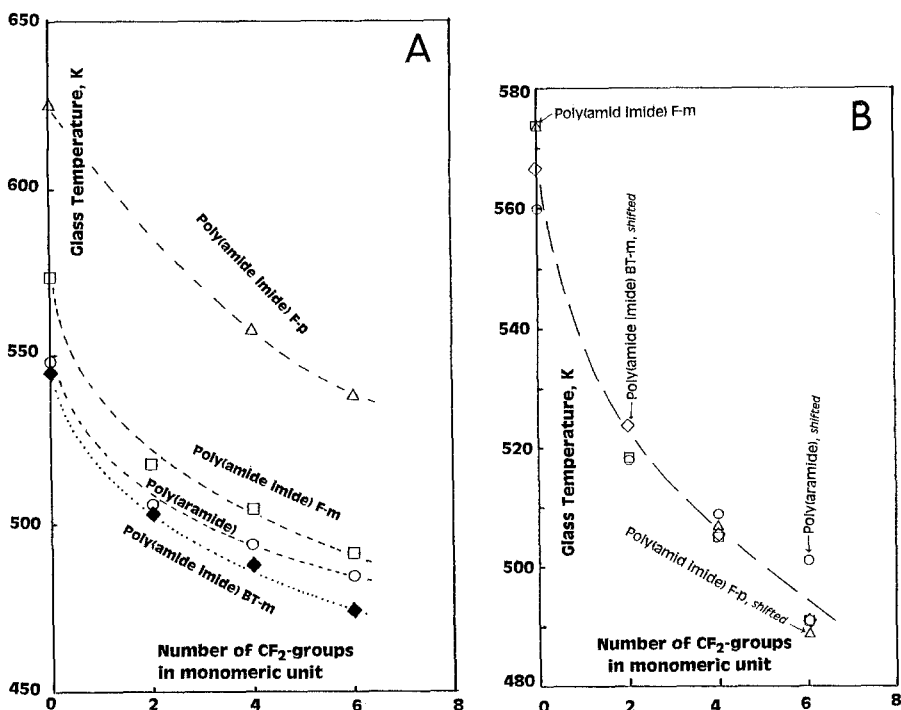


Fig. 1 Influence of the CF_2 -segment length on the glass temperature of poly(aramide)s and poly(amide imide)s
 A. Tg vs. CF_2 -segment length curves
 B. Tg vs. CF_2 -segment length 'mastercurve'

The same decrease of the glass temperature has also been observed in poly(phenylene ether ketone)s after insertion of the same number of flexible phenylene thio ether units in the main chain of different PEK's⁽⁴⁾. Moreover, for side chain polymers, the observed decrease of the glass temperature was also identical for the same spacer length in the different families of poly(methacrylate)s⁽³⁾. In both cases 'master-curves' could be constructed.

In Fig. 2 is presented the glass temperatures of the studied polymers vs. the mass/'flexible bond' criterion of the Schneider - Di Marzio rule⁽⁵⁾. Are included the data of the segmented poly(aramide)s i.e. of the poly(aramide)s obtained by using in the polycondensation reaction mixtures of flourinated and non-flourinated diamines (see Tg data of the poly(aramide)s for $a=0.2$ and 0.5 in Table I).

It is evident the Schneider - Di Marzio rule holds only in a first approximation, i.e. the glass temperature increases with increasing mass/'flexible bond' of the monomeric unit. But the Tg vs. mass/'flexible' bond data are not superposing on a single curve. This implicates that in fact the influence of additional structural parameters or of interaction effects have to be accounted for. An exact evaluation of these parameters is, however, not possible at the moment because of the difficulties encountered in an exact evaluation of the number of flexible bonds.

According to Gibbs - Di Marzio⁽⁶⁾, 'flexible bonds' mean only those simple bonds which by rotation contributes to changes of the conformational structure i.e. of the conformational entropy of the polymer. In aromatic main chain polymers it is thus almost impossible to appreciate exactly whether a simple bond linking phenylene rings to attached groups containing double bonds, like the carbonyl $>C=O$, is stiffened or not by interaction, i.e. if such a bond has to be considered a 'flexible bond'.

For the estimation of the mass/'flexible bonds'-values used in Fig. 2 all simple bonds of the main chain were counted as flexible bonds, irrespective of possible interactions with neighbouring phenylene rings.

Taking into account that the glass temperatures of the para-6F polymers are higher than those of the corresponding meta-6F polymers, it is evident that some additional packing or volume effects have to be considered. These additional volume effects, for instance, can be related to rotation of segments or groups around 'flexible bonds' of the monomeric unit. It can thus be assumed that these revolution volumes have to be as large as more assymetric phenylene rings or other stiff moities of the repeating unit are substituted, contributing

therefor to an 'apparent' increase of the 'free volume', i.e. to a decrease of the glass temperature

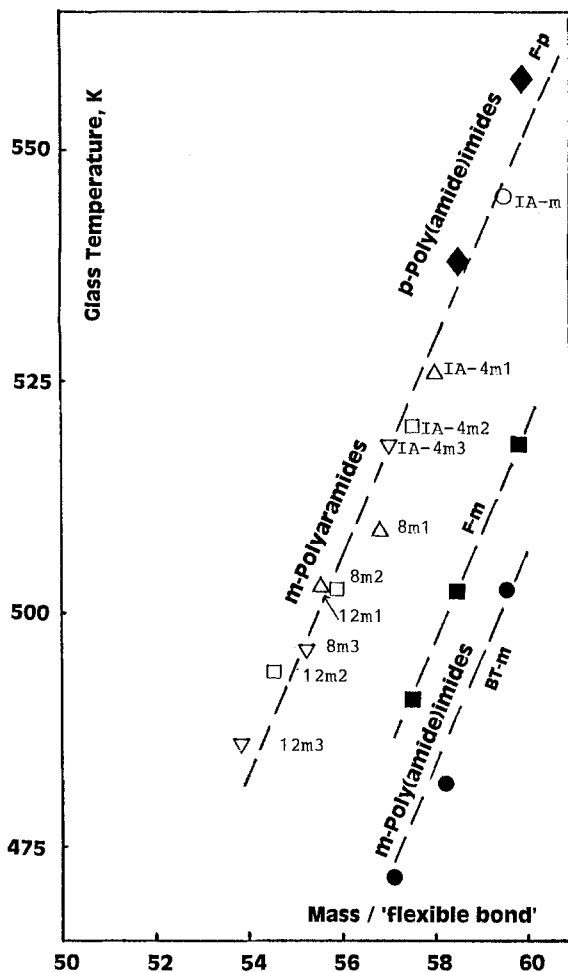


Fig. 2 Glass temperature vs. mass/'flexible bond' of monomeric unit

Open signs - poly(aramides); Full signs - poly(amide imides)
(For significance of the used marks see Tables I and II)

In conclusion, the mass/'flexible' bond criterion of Schneider and Di Marzio allows a rough estimation of the glass temperature characteristic of a given repeating unit. For a more exact prediction of the glass temperature of polymers, however, molecular weight (i.e. end groups) effects, as well as additional 'free' volume effects caused by specific packing and interactions (which contribute to changes of the conformational entropy) have to be considered.

Acknowledgement

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