Synthesis and Characterization of Thermoplastic Graft Copolymer Elastomers with a Polyether Main Chain and Uniform Urethane-Based Side Chains

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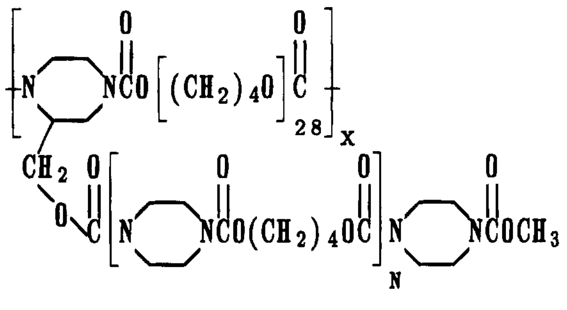
ABSTRACT: The polycondensation reaction of molecularly uniform α,α′-bifunctional oligourethane macromonomers with α-(chlorocarbonyl)-ω-(chloroformyl)poly(oxytetramethylene) yielded graft copolymers with an exactly defined primary structure, i.e., with known graft distribution and length; corresponding oligomeric model compounds were also obtained from the macromonomers by reaction with a monfunctional chain extender. Above a certain length of the side chains the graft copolymers exhibited the typical properties of thermoplastic elastomers. A microphase-separated system was formed in which the grafts have segregated to form semicrystalline hard domains dispersed in a continuous polyether soft phase. The study of the thermal and mechanical properties of these thermoplastic graft copolymer elastomers and their model compounds in comparison with analogously built segmented poly(ether–urethanes) revealed a specific influence of the branching on the packing of the polyurethane grafts and comparable systematics in the elastomer properties with the number of repeat units in the polyurethane graft.

Introduction

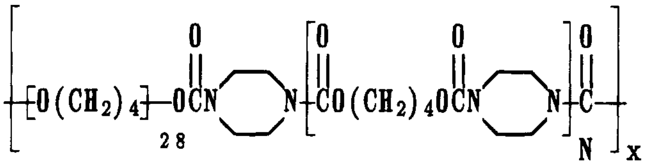
Graft copolymers are comblike branched macromolecules in which the grafted side chains are based on monomeric units different from those of the backbone chain. One reason for the interest in graft copolymers originates from the possible incompatibility of backbone and side chains which can result in intramolecular phase separation; e.g. the side chains can form microdomains dispersed in a continuous phase formed by the backbone.[1] These materials behave as thermoplastic elastomers. Above the glass transition temperature T_g of the continuous phase and below the T_g or melting temperature T_m of the dispersed phase the domains act as thermoreversible, multifunctional cross-links; typical elastomeric properties are observed. Some examples for such thermoplastic graft copolymer elastomers are materials with polystyrene or poly(2,6-dimethyl-1,4-phenylene oxide) grafts and an ethyl or butyl acrylate based backbone,[2–5] with polyester grafts and a poly(ethylene-*co*-propylene-*co*-1,4-hexadiene) or polysiloxane backbone,[6–8] and with a poly(vinyl chloride) backbone and various grafts.[9]

In this paper the synthesis and properties of thermoplastic graft copolymer elastomers (**1a–d**) with a poly(oxytetramethylene) (POTM) backbone and molecularly uniform side polyurethane (PU) chains based on piperazine (PIP) and 1,4-butanediol (BDO)–bis(chloroformate) as well as the corresponding model compounds (**1a–d**) for the grafted side chain will be discussed.



<u>1a</u>: N = 2; <u>1b</u>: N = 3; <u>1c</u>: N = 4; <u>1d</u>: N = 7

The interest turns toward not only the question whether an ordered superstructure is formed by specific interactions between the side chains but also how the properties of the graft copolymers can be compared with those of thermoplastic PU elastomers (**2**)[10,11] with uniform hard segments also based on PIP/BDO–bis(chloroformate) and POTM soft segments (cf. ref 12).



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Experimental Part

Measurements. NMR spectra were obtained with a Bruker AC 250 spectrometer using TMS as the internal standard.

Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer DSC II; cyclohexane, dodecane, benzene, indium, and tin were used as calibration standards, and the sample weight was 2–5 mg.

Dynamic mechanical measurements were carried out with a Brabender torsion automat by using solution ($CHCl_3$) cast films of ca. 10 × 50 × 1 mm size (temperature range 143–450 K, heating rate 1 K/min, frequency ca. 10 Hz).

Gel permeation chromatography (GPC) and HPLC measurements for checking the achieved molar mass of **1a–d** as well as the purity of **6a–d**, **8a–d**, and **11a–d** were carried out as described previously.[13]

Dibenzyl 2-(Hydroxymethyl)-*N,N*′-piperazinedicarboxylate (4). (12.03 g, 0.07 mol) Benzyl chloroformate in 40 mL of dichloromethane, 50 mL of 1.5 N NaOH, and 70 mL of 1 M Na_2CO_3 was simultaneously dropped into a solution of 8.56 g (0.037 mol) of 2-(hydroxymethyl)piperazine (**3**) diacetate[14,15] in 100 mL of dichloromethane. The organic phase was separated after 1 h of stirring, washed, and dried and the solvent removed in vacuo. Yield: 84%. IR (film): 3380 (OH), 1695 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$): δ (ppm) = 2.9–3.2, 3.9–4.3 (2 m; N–CH_2–CH_2–N, N–(–CH)–CH_2–N, 7 H), 3.61 (m; CH_2–OH, 2 H), 5.14 (m; PhCH_2O–, 4 H), 7.34 (m; *Ph*CH_2O–, 10 H).

Dibenzyl 2-[[(Chloroformyl)oxy]methyl]-*N,N*′-piperazinedicarboxylate (5). **5** was obtained in 99% yield by the reaction of 10 g (0.026 mol) of **4** dissolved in 20 mL of $CHCl_3$ with a 5-fold excess of phosgene (from Fa. Messer Griesheim), followed by evaporation of the remaining phosgene. IR

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(film): 1770, 1695 cm^{-1} (C=O). ^{1}H-NMR (CDCl$_3$): δ (ppm) 2.9–3.2, 3.9–4.2 (2 m; N–C*H*$_2$–C*H*$_2$–N, N–(–CH)–C*H*$_2$–N, 6 H), 4.35 (m; C*H*$_2$–O–COCl, 2 H), 4.5 (m; N–(–C*H*)–CH$_2$–N, 1 H), 5.14 (m; PhC*H*$_2$O–, 4 H), 7.34 (m; *Ph*CH$_2$O–, 10 H). ^{13}C-NMR (CDCl$_3$, 25 °C): δ (ppm) 38.6, 39.3 (N–*C*H$_2$–*C*H$_2$–N), 43.1 (N–CH–*C*H$_2$–N), 49.0 (N–*C*H–CH$_2$–N), 65.0 (*C*H$_2$–COCl), 67.6, 67.7 (Ph*C*H$_2$), 127.9, 128.6, 128.9, 136.0 (*Ph*), 150.4 (CH$_2$–O–*C*OCl), 155.1 (PhCH$_2$O–*C*O–).

Methyl Hydro-oligo(1,4-piperazinediylcarbonyloxytetramethyleneoxycarbonyl)piperazine-4-carboxylate (6a–d) were synthesized in a similar way as described earlier.[13]

Methyl 1-[[[[(*N,N*′-Bis(carboxybenzyl)piperazin-2-yl)methyl]oxy]carbonyl]bis(1,4-piperazinediylcarbonyloxytetramethyleneoxycarbonyl)]piperazine-4-carboxylate (7a). A solution of 2.96 g (6.76 mmol) of **5** in 20 mL of dichloromethane was dropped into a solution of 4.1 g (6.83 mmol) of **6a** in 100 mL of dichloromethane, followed by the dropwise addition of 150 mL of 1 M Na$_2$CO$_3$. The organic phase was separated after 1 h of stirring, and the reaction product recrystallized from ethyl acetate. Yield: 72%. IR (KBr): 1695 cm^{-1} (C=O). ^{1}H-NMR (CDCl$_3$): δ (ppm) 1.73 (m; OCH$_2$C*H*$_2$C*H*$_2$CH$_2$O, 8 H), 2.9–3.4 (m; N–C*H*$_2$C*H*$_2$–N–C*H*$_2$–CH, 6 H), 3.46 (s; N(C*H*$_2$–)$_2$, 24 H), 3.71 (s; C(O)OC*H*$_3$, 3H), 4.0 (m; N–CH$_2$CH$_2$–N–CH$_2$–C*H*, 1 H), 4.14 (m; OC*H*$_2$CH$_2$CH$_2$C*H*$_2$O, 8 H), 4.5 (m; >CHC*H*$_2$C(O)N<, 2 H), 5.12 (s; PhC*H*$_2$, 2 H), 7.35 (m; *Ph*CH$_2$, 10 H).

Compounds **7b–d** were obtained from **6b–d** and **5** as described for **7a**; the NMR spectra showed the same signals but different intensities compared to **7a**.

Methyl 1-[[[(Piperazin-2-ylmethyl)oxy]carbonyl]bis(1,4-piperazinediylcarbonyloxytetramethyleneoxycarbonyl)]piperazine-4-carboxylate (8a) was prepared from 5 mmol of **7a** in 100 mL of a 1:1 (v/v) mixture of glacial acetic acid/methanol by catalytic hydrogenation in the presence of Pd/C in a similar way as described earlier.[14] Yield: 68%. IR (KBr): 3326 (N–H), 1689 cm^{-1} (C=O). ^{1}H-NMR (CDCl$_3$): δ (ppm) 1.73 (m; OCH$_2$C*H*$_2$C*H*$_2$CH$_2$O, 8 H), 2.4–3.0 (m; N–C*H*$_2$C*H*$_2$–N–C*H*$_2$–C*H*, 7 H), 3.46 (s; N(C*H*$_2$–)$_2$, 24 H), 3.71 (s; C(O)OC*H*$_3$, 3 H), 4.02 (2 dd; >CHC*H*$_2$C(O)N<, 2 H), 4.14 (m; OC*H*$_2$CH$_2$CH$_2$C*H*$_2$O, 8 H). ^{13}C-NMR (CDCl$_3$): δ(ppm) 25.7 (OCH$_2$*C*H$_2$*C*H$_2$CH$_2$O), 43.5 (N(*C*H$_2$)$_2$), 46.5, 46.6, 49.1, 55.0 (N–*C*H$_2$*C*H$_2$–N–*C*H$_2$–*C*H), 52.8 (C(O)O*C*H$_3$), 65.2 (O*C*H$_2$(CH$_2$)$_2$*C*H$_2$O), 67.7 (>CH*C*H$_2$C(O)N<), 155.0, 155.3, 155.7, *C*O.

Compounds **8b–d** were obtained analogously from **7b–d**; the NMR spectra showed the same signals but different intensities compared to **8a**.

Synthesis of the Graft Copolymers 10a–d. 10a–d were obtained by polycondensation of 1–2 mmol of the macromonomers **8a–d** with **9** in stoichiometric amounts analogously as described earlier for poly(ether–urethane) model elastomers.[11,16,17] The molar masses (number average) of the graft copolymers varied between 30 000 and 35 000 g/mol, as determined by GPC measurements (polystyrene calibration). ^{1}H-NMR (CDCl$_3$, intensities for **10a**): δ (ppm) 1.6 (m; OCH$_2$(C*H*$_2$)$_2$CH$_2$O, ~112 H), 1.72 (m; COOCH$_2$C*H*$_2$C*H*$_2$, 8 H), 2.9–3.4 (m; N–C*H*$_2$C*H*$_2$–N–C*H*$_2$–CH, 6 H), 3.41 (m; OC*H*$_2$(CH$_2$)$_2$C*H*$_2$O, ~112 H), 3.45 (s; N(C*H*$_2$–)$_2$, 24 H), 3.71 (s; C(O)OC*H*$_3$, 3 H), 4.0 (m; N–CH$_2$CH$_2$–N–CH$_2$–*C*H, 1 H), 4.14 (m; OC*H*$_2$CH$_2$CH$_2$C*H*$_2$O, 8 H), 4.5 (m; >CHC*H*$_2$C(O)N<, 2 H).

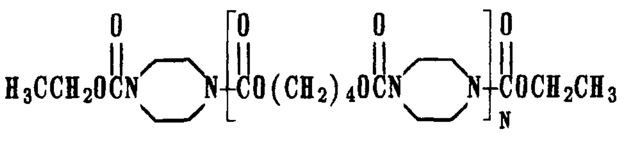
Synthesis of the Oligourethane Graft Model Compounds 11a–d. About 1 mmol of **8a–d** in 10 mL of dichloromethane was charged with 2 mmol (slight molar excess relative to piperazinyl end groups) of 4-methoxybutyl chloroformate (**10**) in 5 mL of dichloromethane followed by the dropwise addition of 15 mL of 1 M Na$_2$CO$_3$ under stirring. The organic phase was separated out, washed, dried, and evaporated in vacuo. The product was purified by recrystallization from chloroform/hexane (1:2 v/v). Yield: about 70%. **10** was obtained analogously as described for **5** and purified by distillation. Bp: 43–45 °C at 0.01 mbar. ^{1}H-NMR (CDCl$_3$, intensities for **11a**): δ(ppm) = 1.73, (m; OCH$_2$(C*H*$_2$)$_2$CH$_2$O, 12 H), 2.9–3.4 (m; N–C*H*$_2$C*H*$_2$–N–C*H*$_2$–CH, 6 H), 3.33 (s; CH$_2$C*H*$_3$, 6 H), 3.39 (t, C*H*$_2$OCH$_3$, 4 H), 3.46 (s; N(C*H*$_2$–)$_2$, 24 H), 3.72 (s; COOC*H*$_3$, 3 H), 4.0 (m; N–CH$_2$CH$_2$–N–CH$_2$–C*H*, 1 H), 4.14 (m; OC*H*$_2$CH$_2$CH$_2$C*H*$_2$O, 12H), 4.5 (m; >CHC*H*$_2$C(O)N<, 2 H). ^{13}C-NMR (CDCl$_3$, 25 °C): δ(ppm) = 25.4, 25.7, OCH$_2$(*C*H$_2$)$_2$CH$_2$O, 38.8, 46.2, N–*C*H$_2$*C*H$_2$–N–CH$_2$–CH, 43.1, N(*C*H$_2$)$_2$, 49.2, N-CH*C*H$_2$N, 52.8, CH$_2$O*C*H$_3$, 61.3, N-*C*HCH$_2$-N, 64.8, 65.0, O*C*H$_2$(CH$_2$)$_2$*C*H$_2$O, 71.5, >CH*C*H$_2$OC(O)N<, 71.7, *C*H$_2$OCH$_3$.

Results and Discussion

The synthesis of graft copolymers with a POTM backbone and monodisperse side chains based on PIP and BDO–bis(chloroformate) is illustrated in the reaction in Scheme 1: The amino groups of 2-(hydroxymethyl)piperazine[14,15] (**3**) are selectively protected by condensation with benzyl chloroformate; the hydroxy group is then converted to the chloroformate **5** by reaction with phosgene. A five-fold excess of phosgene and the reaction conditions, i.e. adding the alcohol to the phosgene and the absence of a base which is required for the formation of a carbonate, guaranteed that no dimerization of **4** occurred; this is confirmed by IR spectroscopy: no carbonate bonds, which could be easily detected also in compounds **7a–d**, are formed. Intermediate **5** is condensed with amino-terminated uniform oligourethanes (**6a–d**), which are accessible from the monomers piperazine, butanediol, and phosgene by a stepwise synthesis using protective groups as described earlier.[11,13,16] The removal of the carboxybenzyl groups by catalytic hydrogenation yields the key intermediates, α,α′-bifunctional macromonomers (**8a–d**) which are reacted with α-(chlorocarbonyl)-ω-(chloroformyl)poly(oxytetramethylene)[11,16] (**9**; starting POTM: $\bar{M}_n$ = 2000 g/mol) to form the graft copolymers (**1a–d**) with an exactly defined primary structure. The overall molecular masses of the graft copolymers are 30 000–35 000 g/mol (GPC, polystyrene calibration), which corresponded to the values x = 9–13 for polymers **1a–d**. With the thermal history depicted in the figures, no backbone crystallization of **1b–d** is observed. Additionally, oligomeric model compounds (**11a–d**) were obtained by the reaction of the macromonomers with 4-methoxybutyl chloroformate.

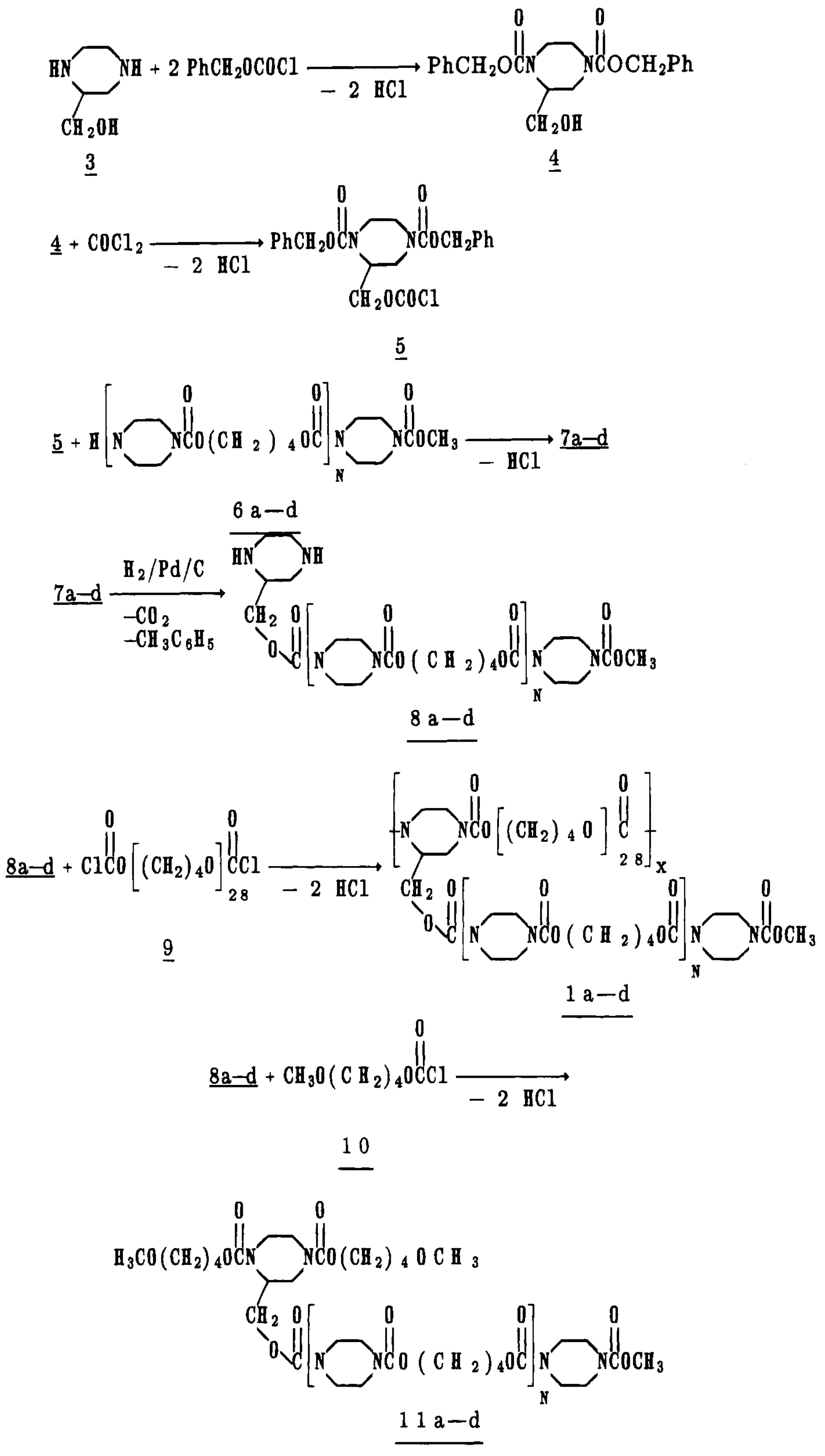
The architecture of the oligomeric model compounds **11a–d** takes into account the special structural features of the graft copolymers: The uniform side chains are represented by oligourethane chains with 1,4-piperazinediylcarbonyloxytetramethyleneoxycarbonyl repeat units and methyl piperazinecarboxylate end groups; the linkage to the polymer backbone is simulated by the methoxybutyl substituents which correspond to the first repeat units of the continuous polyether main chain.

Of special interest is the question, to which extent these model compounds are comparable with linear, molecularly uniform oligourethanes **12** also based on PIP and BDO–bis(chloroformate), which have been investigated as model compounds for the hard segments of the poly(ether–urethanes) **2**.



12, N = 1–7

Scheme 1



5a–8a, 1a, 11a: N = 2; 5b–8b, 1b, 11b: N = 3; 5c–8c, 1c, 11c: N = 4; 5d–8d, 1d, 11d: N = 7

As is seen by analyzing the X-ray scattering data of **11a–b** and **12**,[13] both series of oligourethanes crystallize without chain folding, because a linear increase of the d_{001} spacing with the degree of oligomerization is observed (Figure 1). From the slope of the line a value of 1.13 nm for the repeat units of **12** and 1.17 nm for the repeat units of **11** is obtained, which is in good agreement with the value of 1.16 nm for the 1,4-piperazinediylcarbonyloxytetramethyleneoxycarbonyl repeat unit obtained from a single crystal X-ray analysis of model compounds.[18] Probably due to the voluminous head groups of **11a–d**, their d_{001} spacings are constantly

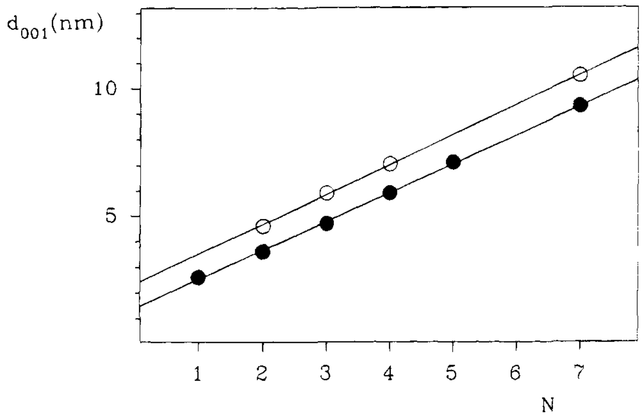


Figure 1. Variation of the d_{001} spacings of **11** (○) and **12**[10,11] (●) as determined by X-ray scattering with the degree of oligomerization N (number of repeat units).

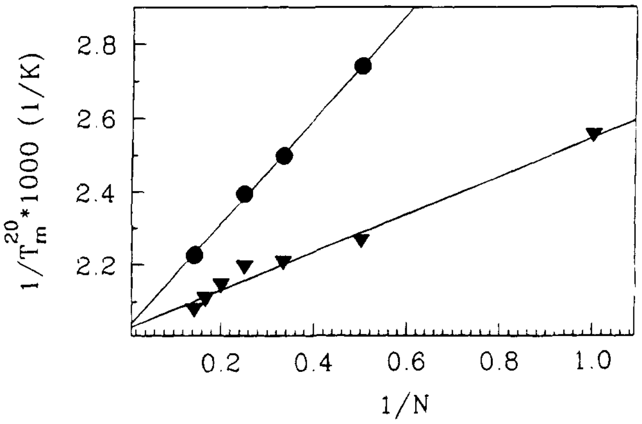


Figure 2. Reciprocal of the melting temperature T_m of **11** (●) and **12**[10] (▼) as a function of the reciprocal of the degree of oligomerization N as determined from DSC (heating rate: 20 K/min).

larger than those of the corresponding oligomers **12** with the same degree of oligomerization.

The position of the melting temperatures of **12** as well as of **11a–d** can be described by means of the Flory–Vrij theory;[19,20]

$$1/T_m = 1/T_m^\infty + 2R/\overline{\Delta H_m}N$$

By plotting the reciprocal value of the melting temperatures T_m versus the reciprocal of the degree of oligomerization N for both **12** and **11a–d** (Figure 2), an equilibrium melting temperature T_m^∞ of 493 ± 3 K is obtained, whereas the melting enthalpy $\overline{\Delta H_m}$ for one repeat unit is 11.6 kJ/mol for **11** and 32 kJ/mol for **12**, respectively. The latter result is in agreement with the experimentally determined melting enthalpies of **11a–d** (Figure 3), which are constantly lower than those of the oligourethanes **12**. As observed for the melting temperatures, the differences between the melting enthalpies decrease with the increasing degree of oligomerization, i.e., chain length.

The results of the thermal and X-ray analyses showed that the properties of the model compounds **11a–d** for the graft copolymers are strongly influenced by the bulky branched end group.

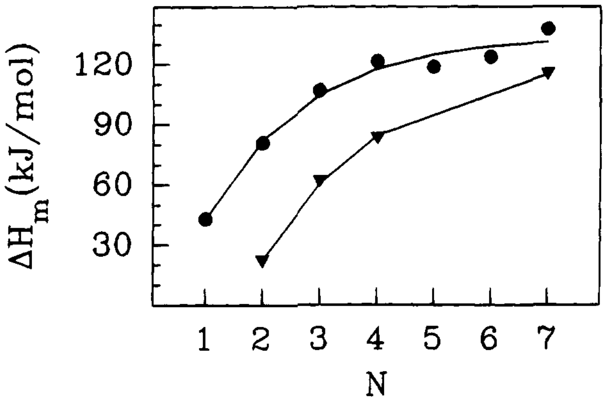


Figure 3. Dependency of the melting enthalpies ΔH_m of **11** (▼) and **12**[10] (●) on the degree of oligomerization N as determined from DSC (heating rate: 20 K/min).

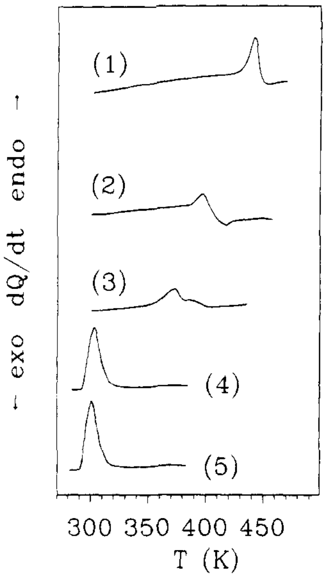


Figure 4. DSC curves of graft copolymer **1** with a polyether main chain and molecularly uniform oligourethane side chains with seven [**1d**, curve 1], four [**1c**, curve 2], three [**1b**, curve 3], and two [**1a**, curve 4] 1,4-piperazinediylcarbonyloxytetramethyleneoxycarbonyl repeat units per side chain and of POTM [M_n = 55 000, curve 5]. All samples were taken from films cast from $CHCl_3$ solution (heating rate: 20 K/min). The curves are normalized to the sample weight.

Depending on their length, the side chains of the graft copolymers **1a–d** segregate to semicrystalline domains. This is shown by the DSC traces in Figure 4: The materials with grafts with three [**1b**, curve 3], four [**1c**, curve 2], and seven [**1d**, curve 1] 1,4-piperazinediylcarbonyloxytetramethyleneoxycarbonyl repeat units are characterized by melting endotherms of which the temperature increases with the increasing length of the side chains. The origin of these endotherms has to be seen in the melting of semicrystalline domains formed by the segregation of the oligourethane grafts. For the material with only two repeat units per side chain (**1a**) one endotherm (curve 4) is observed at the same temperature where semicrystalline POTM (M_n = 55 000, curve 5) melted. This and the relatively strong endotherm compared to the melting of the hard domain of the other graft copolymers implies that the oligourethane grafts of **1a** did not form semicrystalline domains and the endotherm represents the melting of the polyether backbone; this view is supported by the fact that a melting endotherm associated with the melting of hard domains is observed when a spacer is introduced between backbone and graft,[21] although it cannot be completely ruled out that hard domain melting of **1a** may not be detectable in the DSC experiment because of overlaying endotherms. However, since the POTM backbones of all the graft copolymers **1a–d** are of

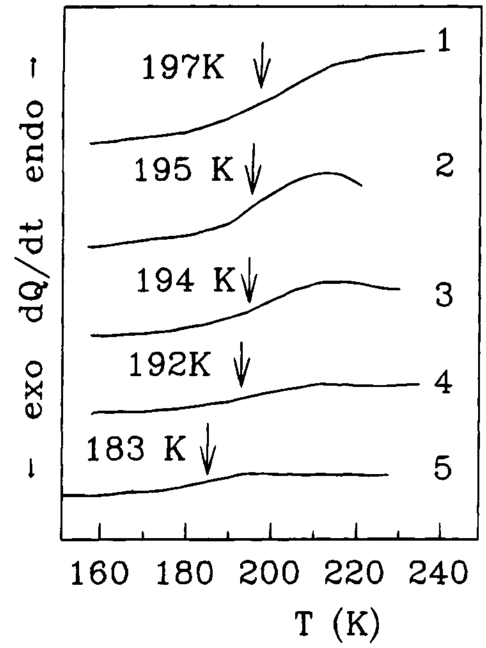


Figure 5. Low-temperature DSC curves of graft copolymers with a polyether main chain and uniform oligourethane side chains with two [**1a**, curve 1], three [**1b**, curve 2], four [**1c**, curve 3], and seven [**1d**, curve 4] 1,4-piperazinediylcarbonyloxytetramethyleneoxycarbonyl-based repeat units per side chain and of POTM [M_n = 55 000, curve 5]. All samples were films cast from $CHCl_3$ solution (heating rate: 20 K/min). The arrows indicate the glass transition temperature T_g.

comparable lengths, backbone crystallinity may be disrupted when microphase separation occurs, which is the case for $N \geq 3$.

Analysis of the low-temperature thermograms of **1a–d** (Figure 5) leads to the conclusion that the oligourethane grafts are partly dispersed in the continuous soft phase formed by the polyether main chain, as the values for the glass transition temperatures (T_g) are shifted to higher values when compared with the T_g of pure POTM. The amount of side chains dispersed in the soft phase can be estimated from the observed T_g by means of the Gordon–Taylor equation[22] originally derived for statistical copolymers (cf. ref 23):

$$T_g = w_1 T_{g1} + w_2 T_{g2}$$

With the weight fraction w_i of the polyether and polyurethane components in the copolymer, T_{g1} = 183 K (T_g of pure POTM, M_n = 55 000 g/mol) and T_{g2} = 303 K (T_g of a polycondensate of PIP and BDO–bis(chloroformate),[11] i.e., of the polyurethane graft), the mole fraction results shown in Table 1 were obtained: in the graft copolymers, up to 50% of the side chains are dispersed in the soft phase (**1a**), and this value decreases to 10% for the sample with the longest side chains (**1d**). These figures are higher than observed for the corresponding linear poly(ether–urethanes) with molecularly uniform hard segments containing the same number of repeat units (cf. refs 24 and 25) and indicate that phase separation is impeded in graft copolymers.

The occurrence of microphase separation, i.e., the existence of hard domains formed by the oligourethane side chains in a flexible amorphous phase formed by the polyether main chain in the case of **1b–d**, is further proved by the dynamic mechanical experiment (Figure 6). The storage modulus G' of **1b–d** shows a temperature dependence characteristic for thermoplastic elastomers. At low temperatures a high modulus (>10^3 N/mm^2) is observed. Above 200 K the modulus decreases, first reflecting the glass transition of the polyether soft phase, then (at 270–300 K) the melting of soft segment crystallites. This decrease is followed by a plateau region (G' = 10^1–10^2 N/mm^2) which is terminated by a sharp decrease of the modulus. This final decrease, reflecting the melting of the oligourethane hard domains is determined by the graft length: with increasing degree of oligomerization the extension of the plateau region increases, which is in agreement with the results of the DSC experiment. The graft

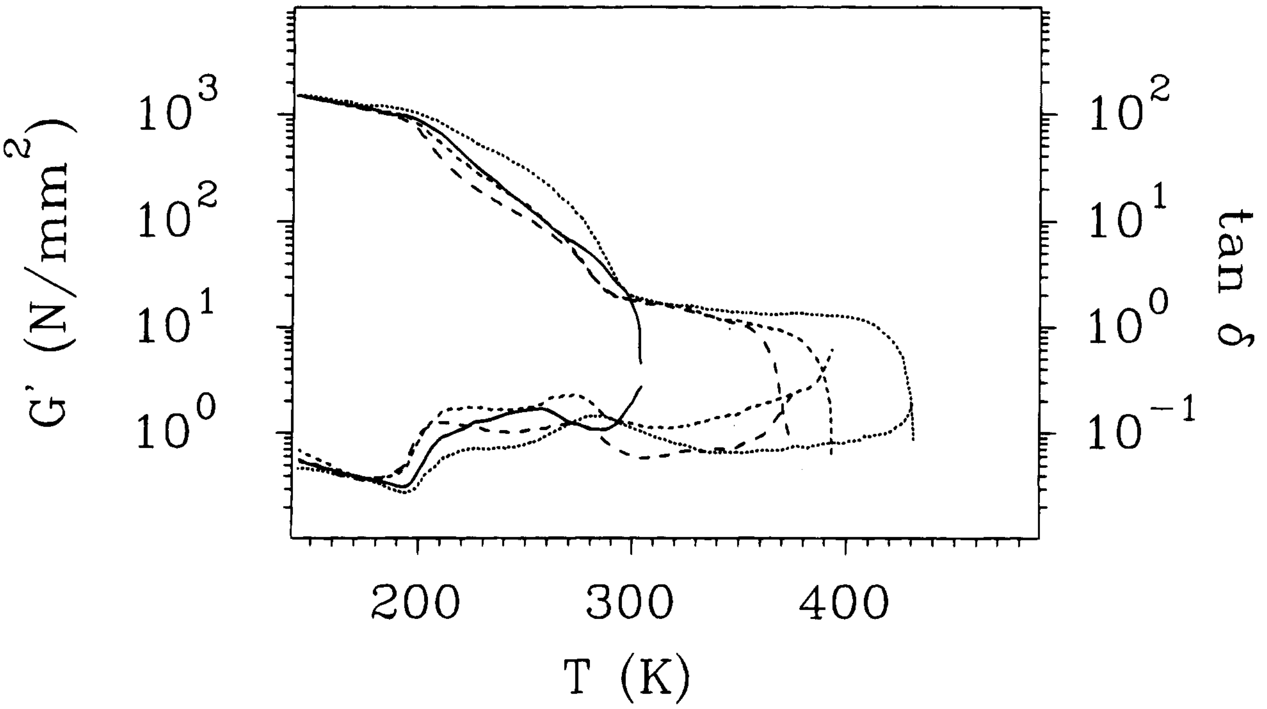


Figure 6. Dynamic mechanical properties of the graft copolymers with a polyether main chain and uniform oligourethane side chains: (—) **1a**; (– – –) **1b**; (- - -) **1c**; (···) **1d**. G': storage modulus. Tan δ: logarithmic decrement.

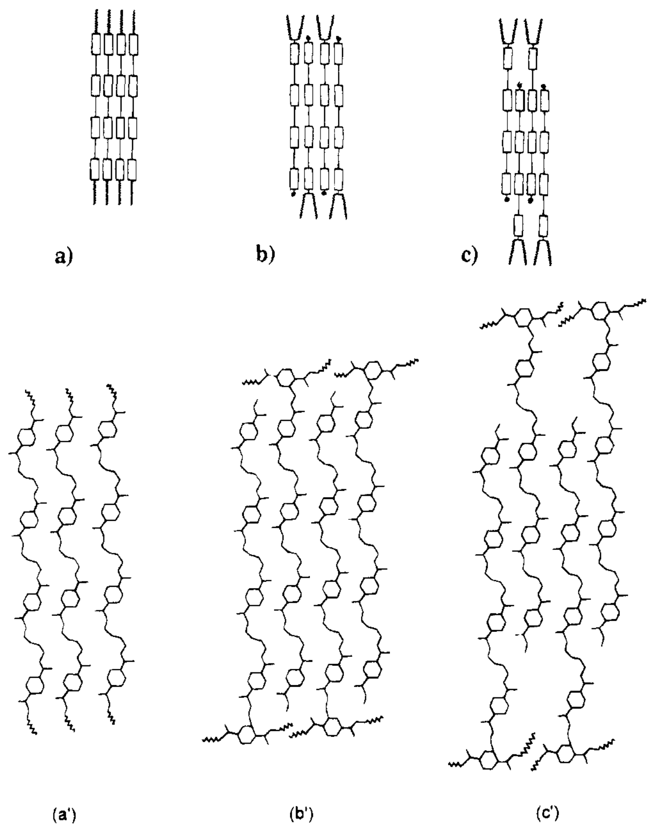


Figure 7. Schematic representation of the packing of the hard segments of the segmented polyurethane elastomer **2** ($N = 3$) (cf. ref 10) (a) and two possibilities (b, c) of the packing of the oligourethane side chains of the graft copolymer **1b**, and a section of the molecular structure and packing of the branching for model b (b′) and model c (c′). Legend: (□) = 1,4-piperazinediyl; (—) = carbonyloxytetramethyleneoxycarbonyl; (—•) = carbonyloxymethyl; (〰) = POTM chain.

copolymer **1a** shows no elastomeric properties: above 200 K a continuous decrease of G' and no plateau region are observed; the material flows after the melting of soft segment crystallites which is in agreement with the DSC data.

A comparison of the PU hard domain melting points of graft copolymers **1a–d** with those of the analogous segmented poly(ether–urethane) multiblock copolymers (**2**)[11] reveals a systematic difference as far as the correlation of the hard domain melting with the number of repeat units in the PU side group or segment is concerned. For a given number of repeat units, the melting temperature of the hard domain of the graft copolymer is always lower than the figure of the multiblock copolymer (Table 2); it is striking that the figures observed for the graft copolymer are relatively close to the melting temperature obtained for the multiblock copolymer with one repeat unit less in the hard segment.

Furthermore, the melting enthalpies of the graft copolymers **1a–d** are clearly lower than those of the analogous segmented elastomers **2** (Table 2), and the differences decrease with the increasing number of repeat units. Again, considering the fraction of polyurethane (graft or segment, respectively) incorporated in the hard domain only, the molar heat of fusion of the PU graft with a given number of repeat units is comparable to the figure obtained for the multiblock copolymer with one repeat unit less in the hard segment.

These findings may be interpreted as follows: In the segmented materials all repeat units of the hard segments can contribute to the formation of hard domains; this is schematically shown in Figure 7a for the example of a perfect hard segment packing forming a sharp phase boundary (cf. ref 11). Obviously, a similar packing model in which all repeat units of the PU side group contribute to the crystalline hard domain, as depicted in Figure 7b, does not apply for graft copolymers because of steric and/or conformational reasons, e.g. as a consequence of steric interactions between the covalently linked polyether main chain which continues to both sides of the graft, and/or confined space for the

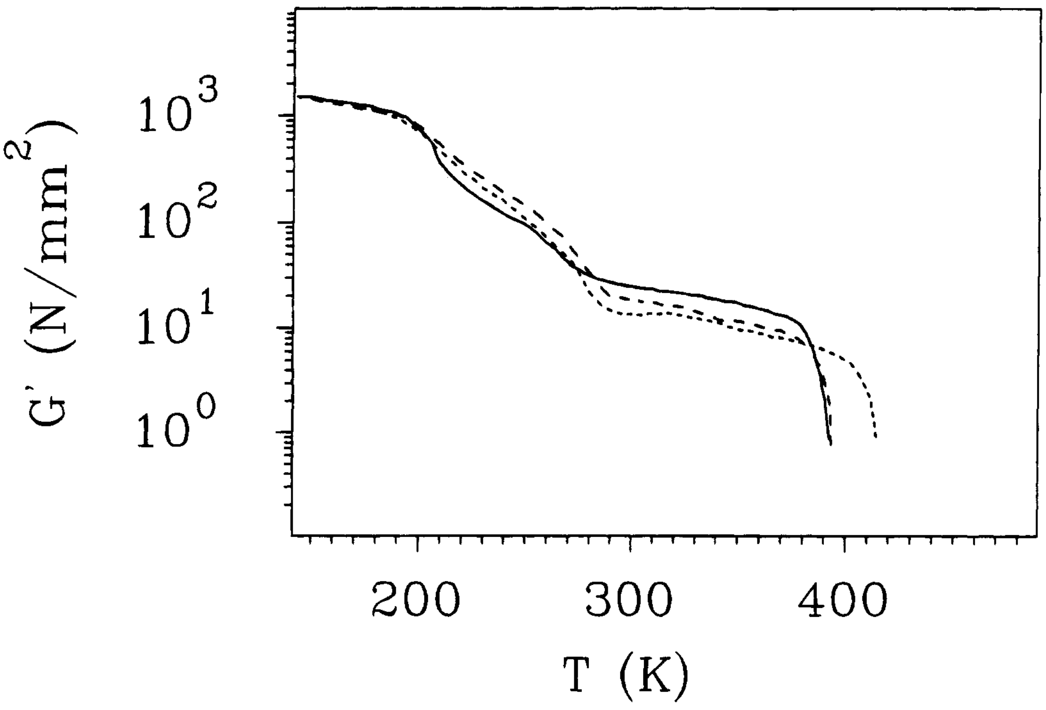


Figure 8. Dynamic mechanical properties of the segmented polyurethane elastomers **2** ($N = 3$, —; $N = 4$, - - -) and of the graft copolymer **1b** with a polyether main chain and uniform oligourethane side chains ($N = 3$, — — —). G': storage modulus.

Table 1. Mole Fractions x_{1s} of the Polyether (POTM) Main Chain in Graft Copolymers 1a–d, Glass Transition Temperatures T_g of the POTM Soft Phase, Mole Fraction x_2 of Polyurethane Grafts Dispersed in the Soft Phase, Mole Fraction x_{2r} of Hard Phase Forming Grafts, and Percent of Dispersed Grafts (% disp) in Relation to the Total Amount of Grafts

polymer	x_{1s}	T_g/K	x_2[a]	x_{2r}	% disp
1a	0.79	197	0.11 ± 0.026	0.10	50 ± 12
1b	0.73	195	0.08 ± 0.022	0.19	30 ± 8
1c	0.68	194	0.07 ± 0.021	0.29	22 ± 6
1d	0.56	192	0.02 ± 0.017	0.42	10 ± 4

[a] The error has been estimated from the inaccuracy in the determination of the T_g values in the DSC traces Figure 2.

Table 2. Melting Temperature T_m and Heat of Fusion ΔH_m of the Graft Copolymers 1 and the Segmented Polyurethanes 2 in Relation to the Number of 1,4-Piperazinediylcarbonyloxytetramethyleneoxycarbonyl Repeat Units in the Polyurethane Graft or Segment, Respectively (First Heating, Heating Rate 20 K/min)

	T_m/K		$\Delta H_m{}^a$/kJ·mol^{-1}	
N	**1**	**2**	**1**	**2**
2	*b*	381		34.3 (51.9)
3	372	414	34.3 (48.9)	70.7 (83.2)
4	398	435	56.3 (72.5)	71.7 (84.2)
5[c]		450		89.9 (105.6)
6[c]		457		105.1 (117.8)
7	442	467	106.9 (119.3)	130.4 (135.8)

[a] Heat of fusion per mole of polyurethane graft or segment in **1** and **2**, respectively. Figures in brackets are corrected for the fraction of polyurethane graft or segment dispersed in the soft phase; i.e., they represent the molar heat of fusion of polyurethane in hard domains. [b] No hard domain melting observed in the DSC trace. [c] These graft copolymer samples were not prepared.

methylurethane end group at the branching. Both the branch end group and the polyether chain at the branching can be accommodated easier in the packing model depicted in Figure 7c, where the first repeat unit of the oligourethane side chain of the graft copolymers next to the polymer backbone has to be regarded as a part of the soft phase.

The overcrowding at the branching in the packing model depicted in Figure 7b is also clearly evident from the corresponding molecular packing model depicted in Figure 7b′ which is based on the crystalline structure of the polyurethane (cf. ref 18). The molecular packing model in Figure 7c′ (corresponding to the schematic picture Figure 7c) illustrates the advantage of the proposed packing of polyurethane side chains in the hard domains of the graft copolymers, the more so if one considers that the rotational freedom of the first oxytetramethyleneoxy constitutive unit after the branching allows a further decrease of the steric interaction of the backbone chains at the branching site.

The interpretation of the melting behavior of the graft copolymers as a consequence of the fact that one repeat unit does not participate in the formation of hard domains, as schematically depicted in Figure 7c, is consistent with the dynamic mechanical measurements, illustrated in Figure 8 for **1c** and the block copolymers **2**, $N = 3$ and 4. The plateau region of the segmented PU elastomer **2** with three repeat units ($N = 3$) in the molecularly uniform hard segment ends at the same temperature where G' of the graft copolymer **1c**, containing one more repeat unit ($N = 4$) in the side chain, finally decreases. The plateau region of **2** with four repeat units ($N = 4$) is clearly extended to higher temperatures until the hard domains melt. The discrepancies between the hard domain melting temperature as determined by DSC and dynamic mechanical testing (Table 2, Figure 7) are due to differences in the measuring methods.

The finding that the characteristics of the graft copolymer architecture, i.e., the linkage of crystallizable grafts and the main chain through branching points, have a definite influence on the macroscopic properties of the polymers is in good agreement with the results of the investigation of the model compounds **11**, where the bulky piperazinediyl “head group” restrains the crystallization, especially of the short oligomers.

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