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Grafting on Poly(ether ether ketone ketone)s (PEEKK) by Anionic Deactivation

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ABSTRACT: A simple method to synthesize new comb-type polymers with a poly(ether ether ketone ketone) (PEEKK) backbone is presented. The central step is the anionic deactivation of the carbonyl groups by living anions of polystyrene (PS) or polyisoprene, resulting in a PEEKK-*g*-polystyrene or PEEKK-*g*-polyisoprene, respectively. Herein, the influence of different degrees of grafting on the polymer properties is studied by DSC measurements. In model reactions it is shown that the addition of small anions to the carbonyl groups occurs quantitatively. However, grafting of the living anion of polystyrene or polyisoprene is limited to a conversion of 30%.

Introduction

Grafting is by far the most important process for chemical modification of known polymers.[1] Graft copolymers are not only interesting on their own because of their physical properties and morphology, but they have also been applied as compatibilizers, coatings, surface modifiers, and adhesives.[2] Their attractivity stems from an easy access and from the broad range of possible comonomers, which allow for considerable tunability of the polymer properties.

Most of the graft copolymers are prepared by a *grafting-from* process wherein the grafting is initiated by a thermal[3] or radiation induced[4] radical formation on the polymer backbone. While these methods are inappropriate for the synthesis of well-defined copolymers for principle reasons,[5] it should be possible to control molecular architecture by using the method of anionic deactivation.[6] Here, a living anionic polymer is reacted with electrophilic functions of another polymer backbone. This procedure is very efficient and reliable, because the high reactivity of carbanions guarantees a maximum grafting. Accordingly, side chains can be attached in a straightforward fashion. Moreover, the graft copolymer, the backbone, and the grafts can be characterized separately, allowing determination of the individual molecular weights and thus of the composition of the copolymer.[7] Even though the distribution of grafts along the backbone is random, one should be able to control the average number of grafts by varying the stoichiometry of the nucleophile.

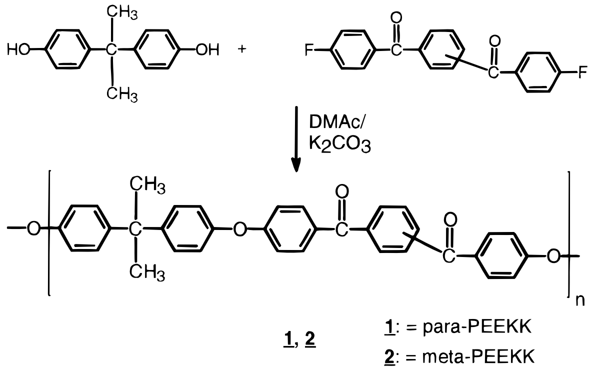
In the present paper, grafting of living anions on poly(ether ether ketone ketone)s is reported. The preparation and characterization of graft copolymers are further supported by suitable model reactions. The effect of grafting on the thermal properties of the copolymers are also discussed.

Experimental Section

General Methods. Monomers were purified according to standard literature procedures.[8] Tetrahydrofuran (THF) was distilled over potassium/benzophenone using a column of at least 1 m length. The *n*-butyllithium (*n*BuLi) concentration was determined by Gilman's double-titration method.[9]

The ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AMX 500 instrument. Molecular weights were determined on a Spectra Physics GPC instrument, relative to polystyrene standards, using THF as an eluent at a flow rate of 1 mL/min; a UV detector was set at 254 nm wavelength. The glass transition temperatures were determined by DSC on either a Mettler TC 10 A or a Mettler TC 11 at a heating rate of 10 K/min under nitrogen, taken as the midpoint of the change in the slope of the baseline.

Scheme 1. Synthesis of PEEKK 1 and 2



Synthesis of PEEKK 1 and 2. Poly(ether ether ketone ketone)s **1** and **2** were prepared according to literature procedures via nucleophilic displacement of aromatic difluorides by Bisphenol-A.[10] The resulting polymers were precipitated from methanol and dried at 100 °C in vacuo.

^{1}H-NMR (200 MHz, CDCl$_3$, δ/ppm) of **1**: 0.81 (t, 3H, methyl), 1.73 (s, 6H, methyl), 7.04 (m, 4H, phenylene), 7.27 (d, 4H, phenylene), 7.84 (m, 8H, phenylene).

^{13}C-NMR (125 MHz, CDCl$_3$), δ/ppm) of **1**: 29.89 (methyl group), 42.3 (quaternary benzylic carbon), 117.82, 120.35, 129.62, 130.15, 131.83, 133.27, (tertiary aromatic carbon), 141.59, 147.05, 153.72, 162.85 (quaternary aromatic carbon), 195.25 (carbonyl carbon).

^{1}H-NMR (500 MHz, THF-d_8, δ/ppm) of **2**: 1.72 (6H, s, methyl groups), 6.97 (4H, d, $^{3}J = 6.8$ Hz, A part of AA′BB′ system), 7.02 (4H, d, $^{3}J = 6.8$ Hz, A part of AA′BB′ system), 7.20 (4H, d, $^{3}J = 6.8$ Hz, B part of AA′BB′ system), 7.60 (1H, t, $^{3}J = 7.5$ Hz), 7.75 (4H, d, $^{3}J = 6.8$ Hz, B part of AA′BB′ system), 7.96 (2H, dd, $^{3}J = 7.5$ Hz, $^{4}J = 1.7$ Hz); 8.13 (1H, t, $^{4}J = 1.1$ Hz),

^{13}C-NMR (125 MHz, THF-d_8, δ/ppm) of **2**: 30.7(methyl groups), 42.1 (quaternary benzylic carbon), 116.9, 119.4, 128.1, 130.4, 132.2, 132.7 (tertiary aromatic carbon), 131.0, 137.9, 146.7, 152.9, 161.8 (quaternary aromatic carbon), 194.2 (carbonyl carbon).

GPC (THF, calibration versus polystyrene standard): $M_n = 15\,000$ g/mol, $M_w = 110\,600$ g/mol. TGA: weight loss, 48% at 488 °C; glass transition temperature, 152 °C (DSC).

Model Reactions. (a) Nucleophilic Addition of Phenyllithium on 2. 2 (2 mmol, (1.02 g) was dissolved in 20 mL of THF and cooled to 0 °C. After the addition of 8 mmol of phenyllithium (1.8 M in THF), the mixture was stirred for 30 min at 0 °C and then quenched by the addition of 1 mL of

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methanol. The resulting polymer was precipitated from aqueous methanol. After reprecipitation from THF/aqueous methanol, the polymer was dried at 50 °C in vacuo. Polymer **3** was obtained in quantitative yield.

^{1}H-NMR (500 MHz, THF-d_8, δ/ppm) of **3**: 1.63 (6H, s, methyl groups), 5.40 (2H, d, alcohol protons), 6.80 (4H, d, $^3J = 8.5$ Hz, A part of AA′BB′ system, H_f), 6.84 (4H, d, $^3J = 8.5$ Hz, A part of AA′BB′ system, H_a), 7.10−7.31 (19H, H_b, H_d, H_e, H_g, H_h, H_i), 7.40 (2H, t, $^3J = 6.3$ Hz, H_j), 7.60 (2H, d, $^3J = 8.5$ Hz, H_c).

^{13}C-NMR (125 MHz, THF-d_8, δ/ppm) of **3**: 31.4 (methyl groups), 42.7 (quaternary benzylic carbon), 81.5 (trityl carbon), 118.1, 118.9, 126.4, 127.0, 127.1, 127.6, 127.6, 127.8, 128.7, 129.4, 130.3, 131.1(tertiary aromatic carbon), 142.0, 143.90, 143.95, 146.3, 148.2, 149.08, 149.01, 156.1, 156.9 (quaternary aromatic carbon).

TGA: weight loss, 17% at 131 °C; 8% at 301 °C; 68% at 520 °C; glass transition temperature, 90 °C (DSC).

(b) Synthesis of 6a and 6b by the Nucleophilic Addition of Polystyrene (PS) Monoanion on Diketone 5. THF (20 mL) was distilled into a thoroughly dried flask and flushed with argon. At −78 °C living polystyrene was prepared from 29 mmol of styrene (3 g) using *n*BuLi as initiator. After stirring for 15 min at −78 °C, a sample of the living anion was taken to determine the molecular weight of the polystyrene side chains. A calculated amount of diketone **5** dissolved in THF was added to the residual mixture to yield **6a** or **6b**. The mixture was stirred for 2 h at −78 °C and quenched by the addition of 1 mL of water. After warming to room temperature, polymers **6a,b** were precipitated by pouring into 300 mL of methanol, dissolved in THF, precipitated again in methanol, and dried at 50 °C in vacuo.

6a: addition of 1 equiv of diketone **5**; $M_n = 3300$ g/mol, $M_w = 6300$ g/mol; $T_g = 92$ °C

6b: addition of 0.5 equiv of diketone **5**; $M_n = 6200$ g/mol, $M_w = 9600$ g/mol; $T_g = 92$ °C.

Synthesis of PEEKK-*g*-polystyrene and PEEKK-*g*-polyisoprene. THF (20 mL) was distilled into a thoroughly dried flask flushed with argon. At −78 °C, living polystyrene was prepared from 29 mmol of styrene (3 g) using *n*BuLi as initiator. After stirring for 15 min at −78 °C, a sample of the living anions was taken to determine the molecular weight of the polystyrene side chains. A calculated amount of **2** dissolved in THF was added to the residual mixture. The clear solution was stirred for 2 h at −78 °C and quenched by the addition of 1 mL of water. After warming to room temperature, the graft copolymers were precipitated by pouring into 300 mL of methanol. The colorless precipitates were washed with methanol and boiled in acetone to remove unreacted polystyrene. The residual polymer was dried, dissolved in THF, precipitated again in methanol, and dried at 50 °C in vacuo.

PEEKK-*g*-polyisoprene was prepared in a similar way, but precipitation from ice-cold aqueous methanol was used.

Results and Discussion

As outlined above, anionic deactivation is the method of choice for preparing well-defined graft copolymers. In principle, this process involves the nucleophilic addition of highly reactive anions to suitable functional groups on the polymer backbone.[11] The carbonyl group appeared as an ideal target because of its high reactivity, which provides selective addition under formation of tertiary alcohols. Therefore, we chose poly(ether ether ketone ketone)s **1** and **2** as polymers for anion deactivation.

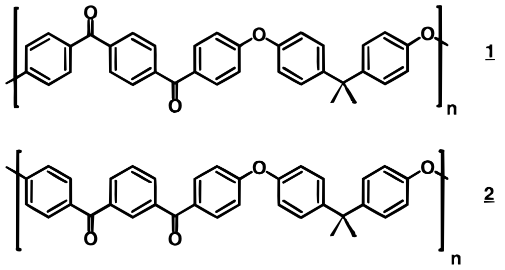
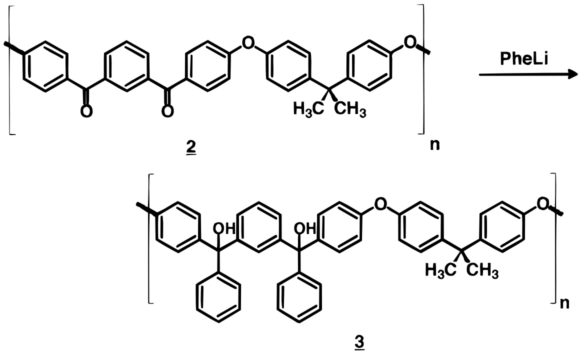


Figure 1. Poly(ether ether ketone ketone)s **1** and **2**.

Scheme 2. Synthesis of 3 by the Anionic Deactivation of 2 with Phenyllithium



It appears in the course of the grafting experiments that the para derivative **1** is not suitable for the desired reaction. After adding the living anion of polystyrene to the solution of **1** in THF, the color of the mixtures changes immediately to deep blue. This color change may be caused by the formation of ketyl radicals. To support this explanation, we determined the redox potentials of polymers **1** and **2** via cyclic voltammetry.[12]

For polymer **1**, we observed a redox potential of −1.60 V vs SCE and for polymer **2**, a value of −1.84 V vs SCE, which means the conjugated electron-withdrawing carbonyl groups in the para-linked dibenzoylbenzene subunit of polymer **1** increase the redox potential. Therefore, we conclude that **1** does not undergo nucleophilic addition with electron-rich carbanions such as poly(styryllithium). Instead, single electron transfer (SET) is favored, yielding mixtures of styryl and blue ketyl radicals.

However, in PEEKK **2** the conjugation is interrupted by the meta topology of the dibenzoylbenzene unit. The effective π-system is reduced and the redox potential lowered. The shift of 240 mV is sufficient to suppress the SET as a competing process.

Model Reactions. In a model reaction, **2** was treated with an excess of phenyllithium, yielding the corresponding poly(ether alcohol) **3** (Scheme 2).

Here it is important to note that the poly(ether ether ketone ketone) **2** is quantitatively transformed into poly(ether alcohol) **3**; no keto groups remain as demonstrated by the shift of the signals in ^{1}H-NMR spectra (Figure 2).

In general, resonances are shifted toward higher fields, which can be easily explained by the increasing electron density due to the chemical transformation of the electron-withdrawing carbonyl group. Most characteristic are absorptions of OH protons at $\delta = 5.4$, which are observable in THF but vanish if small amounts of D_2O are added. In the aromatic region, H_a and H_f appear at higher field, comparable to the corresponding protons of **2**. Protons H_b, H_g, H_d, and H_e and protons of added phenyl rings cannot be resolved but are found as a multiplet in the range $\delta = 7.10$−7.31. The effects due to the addition of phenyl groups are most clearly detected in the central part of the isophthalophenone unit; thus, the doublet due to H_c's is shifted from $\delta = 7.96$ to $\delta = 7.60$, and H_d experiences the largest shift by 0.8.

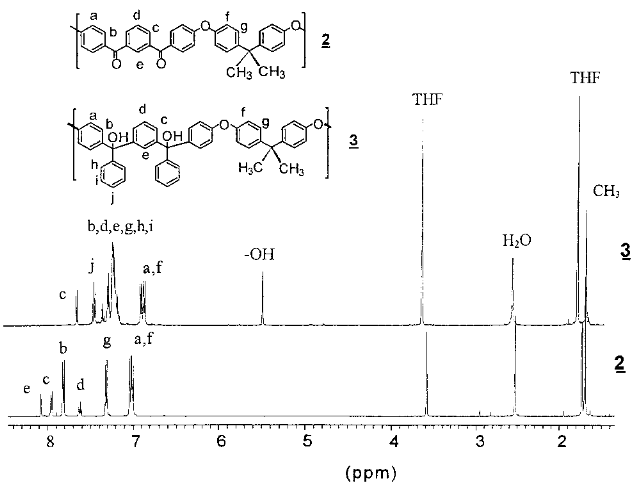


Figure 2. ^{1}H-NMR spectra of **2** and **3** (500 MHz, THF-d_8).

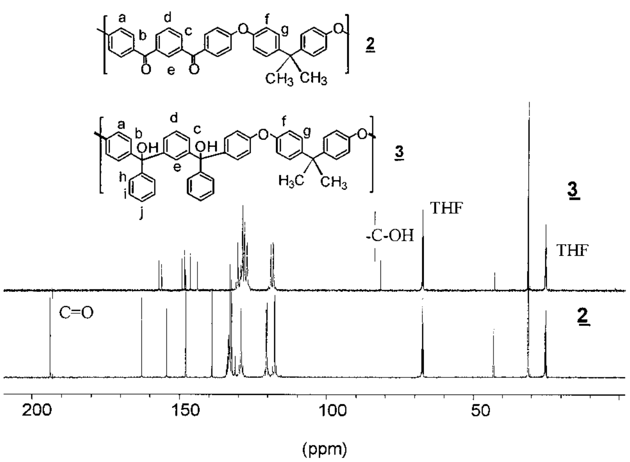


Figure 3. ^{13}C-NMR spectra of **2** and **3** (125 MHz, THF-d_8).

Further support for the complete transformation of the carbonyl groups is obtained by ^{13}C-NMR spectra. The low-field resonances of the carbonyl groups have completely disappeared, while the newly formed quaternary carbon atoms absorb at $\delta = 81.5$.

The conclusion emerging from these experiments is that the reactivity of the keto functions is not severely affected by their incorporation into the polymer backbone. Furthermore, monofunctionalization of a repeat unit does not suppress the reactivity of the remaining carbonyl group. One anticipates, therefore, that a high degree of grafting is accessible in the transformations of **1** and **2**.

In a second model reaction, PEEKK **2** was replaced by a model diketone **5**, but now living polystyrene was used as a nucleophile. If the nucleophilic addition occurs quantitatively, one would expect the following outcome: reaction of 1 equiv of living anions with 1 equiv of **5** should yield polystyrene with the same molecular weight relative to the living anions, while a polystyrene with double molecular weight is expected, if only 0.5 equiv of **5** is added.

As shown in Table 1, it is indeed possible to control the molecular weight of the resulting polymers by a proper choice of the stoichiometry. If one diketone is added per living anion, the number-average molecular weight of the material **6a** remains unaffected. However, an increase of the polydispersity is observed, due to the fact that under the reaction conditions a mixture of unreacted **5** and of molecules with one or two attached polystyrene chains arises. If the number of available keto groups is reduced, two living anions have to attack the same molecule, and the product **6b** exhibits twice the molecular weight of one polystyrene chain.

Scheme 3. Anionic Deactivation of Diketone 5 by the Living Anion of Polystyrene

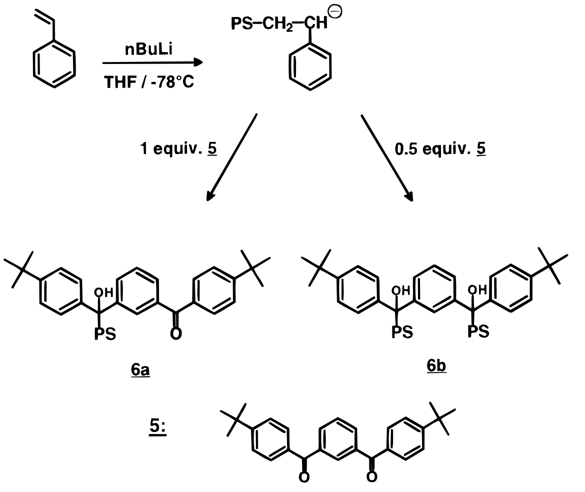
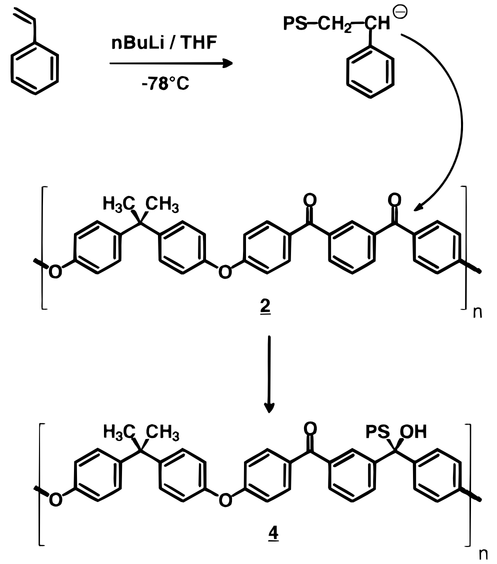


Table 1. Molecular Weights of Model Polystyrenes 6a and 6b

sample	equiv of **5**	M_n (g/mol)	M_w (g/mol)	M_w/M_n
polystyrene		2200	2800	1.3
6a	1	3300	6300	1.9
6b	0.5	6200	9600	1.5

Scheme 4. Grafting of Polystyrene on PEEKK 2 by Anionic Deactivation



Polystyrene as Grafts. Styrene was chosen as a first side-chain comonomer. As is well known, living polystyrene can be readily prepared by living anionic polymerization at low temperatures in THF.[13] THF has to be used as a solvent because of the poor solubility of **2** in aliphatic or aromatic hydrocarbons. Reaction of poly(styryllithium) with **2** yields graft copolymers **4** as colorless powders (Scheme 4).

In contrast to **2**, the resulting polymers **4a**–**c** are completely soluble in 2-butanone, indicating a high degree of grafting. Small amounts of unreacted polystyrene were quantitativly removed by extraction in boiling acetone. This is proven by GPC measurements. Therein no low molecular weight fraction corresponding to polystyrene was detectable. Data of several graft

Table 2. Molecular Weights, Conversion Rates, and T_g's of 2, Polystyrene, and PEEKK-*g*-polystyrenes 4a−c

sample	ratio of PS vs keto groups in reacn mixture	M_n (g/mol)	M_w/M_n	conv of keto groups (%)	ω(PS) (%)	T_g (DSC) (°C)
PS		3 200	1.1		100	90
2		15 000	6.7		0	152
4a	1:1.2	52 000	2.1	28	71	90
4b	1:0.3	42 200	2.3	21	65	92
4c	1:0.2	30 500	2.1	12	51	90 and 149

copolymers obtained by the variation of stoichiometry are outlined in Table 2.

^{1}H-NMR spectra of the samples display the characteristic features of polystyrene. There are two absorptions at high field ($\delta = 1.69$ and 1.87) due to aliphatic protons and two in the aromatic region at $\delta = 6.53$ (ortho) and $\delta = 7.07$ (meta and para). Because of the low ratio of PEEKK protons relative to polystyrene protons, spectra are dominated by polystyrene. Absorptions of the backbone can only be resolved with poor signal-to-noise ratio. In particular, it is not possible to detect the newly formed quaternary carbon atoms in the ^{13}C-NMR spectra, which are thus of only limited value for the structural elucidation of the graft copolymers.

Molecular weights, as given in Table 2, were obtained via GPC. Number-average molecular weights were also measured by membrane osmometry, although a standard polystyrene calibration was used for GPC measurements.[14] Due to the fact that **4** and **7** are hyperbranched polymers, one could expect smaller molecular weights by GPC measurements in comparison to membrane osmometry. However, the deviations of both results are small.[15]

For samples with up to 12% conversion of keto groups (sample **4c**), DSC curves reveal two glass transitions, one due to the backbone and one due to the side chains.

Samples with a high degree of grafting (**4a** and **4b**) display only one glass transition temperature, which is identical to that of polystyrene. Chain mobility is thus determined by side chains only and the formation of a single phase. In contrast, blends of polystyrene and **2** with the same weight percentage of the two components exhibit two glass transitions, identical to the corresponding homopolymers. This can be explained by an incompatibility of the homopolymers. Therefore, it is obvious that the unique possibility to control grafting by stoichiometry also offers control of dynamic and thermal properties and thus of bulk properties of the graft copolymers.

Three findings are noteworthy:

1. Even when using a large excess of poly(styryllithium), no more than 28% of keto groups can be reacted, which represents the maximum degree of grafting. As borne out by the model reaction, this cannot be due to electronic effects but must be caused by steric reasons. Suppose a few side chains have been attached to the backbone; then further living anions have to diffuse against a large local concentration of polystyrene surrounding the backbone. At a certain level of grafting, all remaining keto groups are shielded against further addition by polystyrene chains.

2. If the molar ratio of poly(styryllithium) versus PEEKK is kept below the above limit, one can control the degree of grafting. The amount of reacted keto groups tends to be always somewhat lower than the calculated one, which is caused by traces of water quenching some of the living anions; it is obvious, on the other hand, that the average number of grafted keto groups and the molecular weight of the graft copolymers can be controlled by the stoichiometry. Consequently, this grafting procedure offers the unique possibility to modify the chemical composition of the copolymer and thus the physical properties in a controlled manner by simply varying the molar ratio of the electrophilic and nucleophilic components.

3. Important information regarding dynamic properties, e.g., chain mobility, can be gathered by determination of glass transitions via DSC measurements (Figure 4).

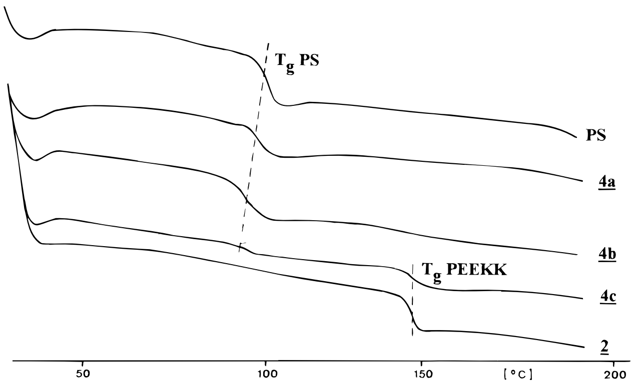


Figure 4. DSC measurements of polystyrene, **2**, and **4a−c**.

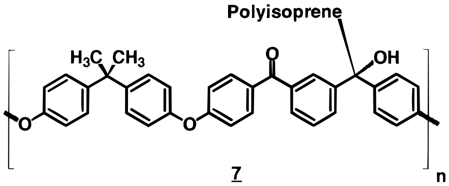


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Figure 5. PEEKK-*g*-polyisoprene **7**.

Polyisoprene as Grafts. Isoprene was chosen as a second comonomer in order to test whether the present method of grafting is generally applicable to the olefins which can be polymerized anionically. Therefore we synthesized PEEKK-*g*-polyisoprene **7**.

Polyisoprene is somewhat different from polystyrene because it appears in at least four different microstructures. Besides trans-1,4 and cis-1,4 insertions, which are most probable in apolar aliphatic solvents, 3,4 or 1,2 addition may also occur. Polymerization of isoprene in heptane yields 70% cis-1,4, 22% trans-1,4, and only 7% 3,4 addition, while a change of the solvent to THF reverses the probability, resulting in 75% 3,4, 6% 1,2, and 18% 1,4 units.[16] As already mentioned, one is restricted to THF as a solvent for grafting on **2**. Therefore, mainly 3,4 connections are expected.

The chemical shifts of the resonances of the protons in the polyisoprene side chains observed in the ^{1}H NMR-spectra of polymer **7** (Figure 5) closely correspond to those published by Bovey for homopolysisoprene.[17] Resonances at $\delta = 5.6$ are due to vinylic protons of 1,4 linkages, while vinyl protons of 3,4 or 1,2 units absorb at $\delta = 4.5$ and 4.9, respectively. The relative signal intensities reveal that the material contains 33% 1,4 units, while the remaining part incorporates 3,4 and of 1,2 structures in a 4:1 ratio.

An interesting case can be made when comparing the conversion rates with those obtained for polystyrene grafts (see Table 3). There is a maximum degree of grafting, which corresponds to 32% conversion of carbonyl groups; and again, it is possible to control the average degree of grafting by simply changing the stoichiometry. Thus, the concept of controlling the

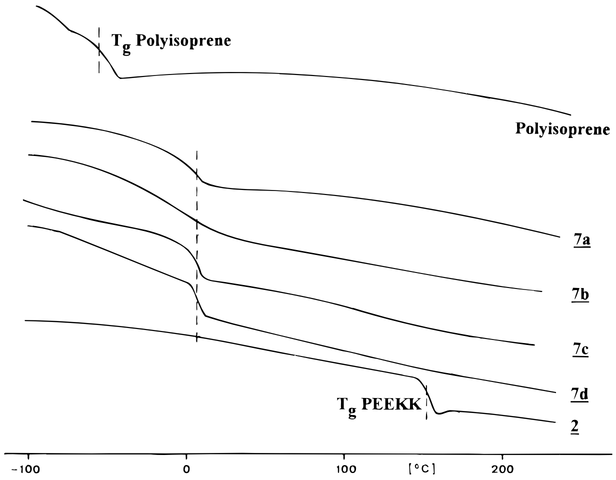

Figure 6. DSC measurements of polyisoprene, **2** and **7a**−**d**.

Table 3. Molecular Weights, Conversion Rates, and T_g's of 2, Polyisoprene, and PEEKK-*g*-polyisoprenes 7a−d

sample	ratio of PI vs keto groups in reacn mixture	M_n (g/mol)	M_w/M_n	conv of keto groups (%)	ω (PI (%))	T_g (DSC) (°C)
PI		3700	1.1			−48
2		15000	6.7			152
7a	2:1	81200	2.9	32	81	−2
7b	0.3:1	61800	2.8	23	76	0
7c	0.2:1	43000	2.6	14	65	−2
7d	0.15:1	34700	3.4	10	57	−2

structure and properties by anionic deactivation can be transferred to other comonomers.

Inspection of glass transitions (Figure 6) exhibits remarkable differences. Whereas the thermal behavior of polystyrene grafts changes with the degree of grafting, this does not hold for the isoprene case. The glass transition of the side chains is raised by 50 °C, which clearly reflects the restricted mobility of the flexible side chains. It does not vary, however, if the average number of grafts per main chain is changed. Nevertheless, the shift from −48 to −2 °C emphasizes the extraordinary consequences of attaching mobile isoprene chains to a PEEKK backbone.

Conclusions

The present paper reports graft reactions via anionic deactivation. To combine the extraordinary properties of a high-performance polymer with those of standard polymers, polystyrene and polyisoprene were grafted on a poly(ether ether ketone ketone) backbone. The high reactivity of the backbone carbonyl groups and the smooth grafting via nucleophilic attack provide graft copolymers with a defined structure, which can be characterized in a straightforward way. The number-average molecular weight of side chains and of the backbone and the average number of grafts per main chain are available. It also appears that the structure and properties of the graft copolymers can be controlled by the stoichiometry of the two components. With a low amount of poly(ether ether ketone ketone), the glass transitions of polyisoprene can be increased. The consequences of grafting on the dynamic behavior of the polymers was monitored by DSC and reveals principal differences between polystyrene and polyisoprene grafts. To explain this behavior further,investigations concerning the morphology and the mechanical properties of the title systems are underway. Additionally, the universal concept of anionic deactivation will be extended to other poly(ether ketone)s and to other monomers polymerizable via anionic polymerization.

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