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Stable Carbanions by Quantitative Metalation of Cationically Obtained Diphenylvinyl and Diphenylmethoxy Compounds: New Initiators for Living Anionic Polymerizations

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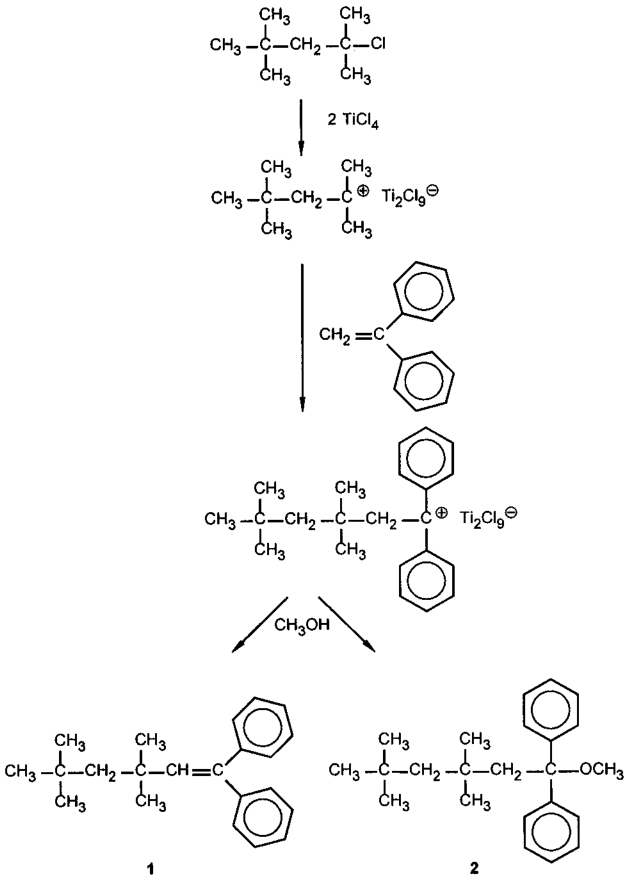
Introduction

Living polymerizations have been the subject of increasing interest in both academia and industry in recent years. Significant efforts have been made to search for new initiating systems which provide quantitative initiation and thus control of the microstructure of the resulting polymers with high precision. Such macromolecular systems with controlled architecture and properties are of great interest not only for material science investigations but also in the development of new specialty products and commodity polymers. In the last decade, the progress in this field has resulted in the expansion of chemical reactions suitable for living polymerizations, for example, by group transfer, cationic, ring-opening metathesis, and free radical mechanisms, in addition to living anionic polymerization which has already existed for more than 40 years (see, e.g., refs 1−9 for recent reviews). Conceptually, it is expected that combining the new controlled quantitative reactions and polymerizations offered by these processes in a designed manner may result in a large variety of new compounds and well-defined polymeric systems, not available in the past.

In the anionic polymerization of polar monomers, e.g., methacrylates or vinylpyridines, the size of the counterion is of great importance for controlling the tacticity and the molecular weight distribution (MWD) of the obtained polymers.[10,11] For instance for the living anionic polymerization of *N*,*N*-dimethylacrylamide only Cs^+ leads to narrow MWD.[12] In addition, initiators with reduced nucleophilicity (e.g., diphenylalkyl anions) are necessary for methacrylates. Monofunctional initiators with large counterions and reduced nucleophilicity are not easily available. Metalation of diphenylmethane with K/Na alloy or with Cs is very slow and not quantitative. Initiation with fluorenyl-Na and -K is slow compared to propagation.[13] In this article we present a quantitative and fast synthesis of a novel initiator with free choice of the counterion (Li^+ to Cs^+) and high initiator efficiency for anionic polymerizations of polar monomers. Moreover, the initiator is a model of polyisobutylene-based macroinitiators, which extends the opportunities for preparation of block copolymers by combination of living cationic and anionic polymerizations.

Experimental Section

Scheme 1. Synthesis of 1 and 2



1 and **2** were obtained as described.[16,17] Metalation of these compounds was carried out by adding a dry THF solution of **1** or **2** ($1.5-4 \times 10^{-3}$ M) to a flask containing excess K/Na alloy (3−5:1 w/w), Cs metal or Li dispersion in a glovebox under dry N_2. At predetermined times, samples were withdrawn by a syringe, filtered, and quenched with degassed methanol.

When the metalation was carried out by K/Na alloy, the corresponding Li salt was obtained by adding ~10 times excess of LiCl to the reaction mixture (**1** or **2** and K/Na) leading to the formation of insoluble KCl. Subsequently, the polymerization was started by charging the monomer in bulk at −78 °C. The polymerization was quenched with methanol, then the solvents were removed by rotavap, and finally the resulting polymer was dried under high vacuum. The UV measurements were carried out in flask to which a UV cell with spacer (effective path lengh, 0.05 cm) is attached.

Characterization. Size exclusion chromatography (SEC); eluent, THF; detectors, 2 x JASCO-UVIDEC 100 III with variable wavelength, Bischoff RI detector 8110; columns, PSS SDV-gel 5 μ, 60 cm, 1x linear (10^2-10^5 Å), 1x 100 Å; calibrations were performed using PIB, PMMA, and PtBMA standards. ^1H NMR 200 MHz; solvent, $CDCl_3$ on a Bruker AC-200 spectrometer.

Results and Discussion

Recently, it has been found[14−17] that tertiary chlorine containing compounds and polymers, e.g., polyisobutylene (PIB), obtained by living carbocationic polymerization can be quantitatively reacted with 1,1-diphenylethylene (DPE) in the presence of Lewis acids, such as BCl_3 and $TiCl_4$. In these cationic reactions, only monoaddition of DPE occurs due to the fact that this compound is a non-homopolymerizable olefin. Depending on the reaction conditions 2,2-diphenylvinyl (DPV) or 1-methoxy-1,1-diphenylethyl (MDPE) groups are formed after quenching with methanol.[17] When 2-chloro-2,4,4-trimethylpentane (TMPCl), a model compound for polyisobutylene chain ends in living cationic polymerization of isobutylene,[5,18] is reacted with DPE, either 3,3,5,5-

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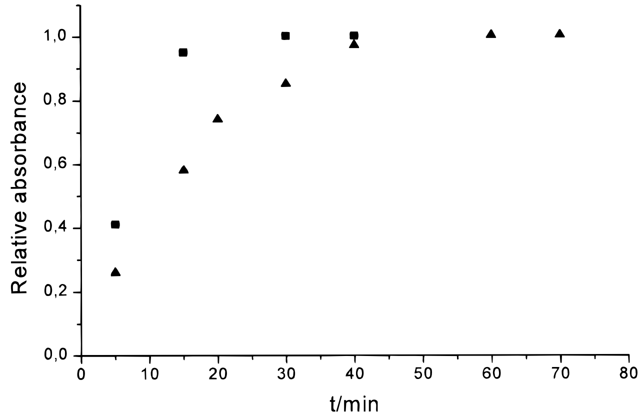
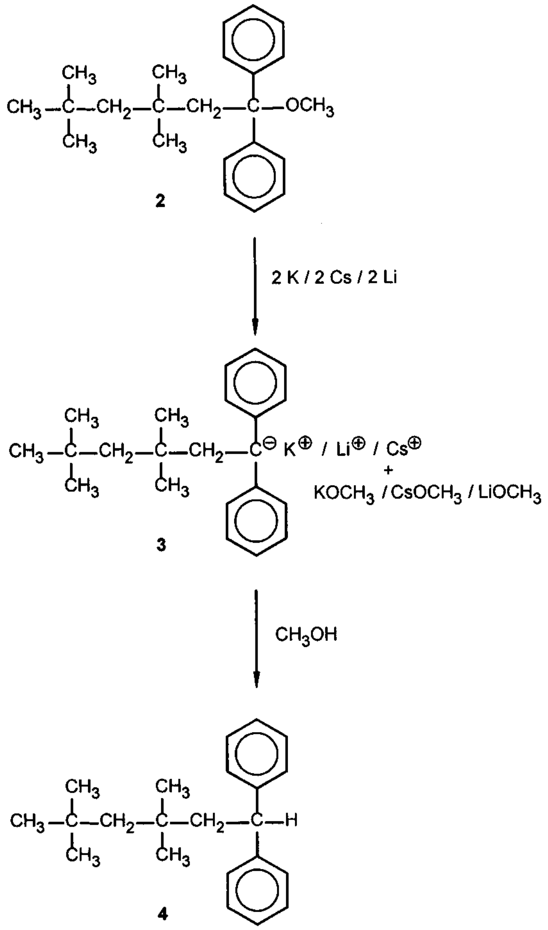


Figure 1. Relative UV absorbance (at $\lambda_{max} = 477-480$ nm) as a function of time during metalation of **2** with potassium/sodium alloy (■) and cesium metal (▲).

Scheme 2. Metalation of 2



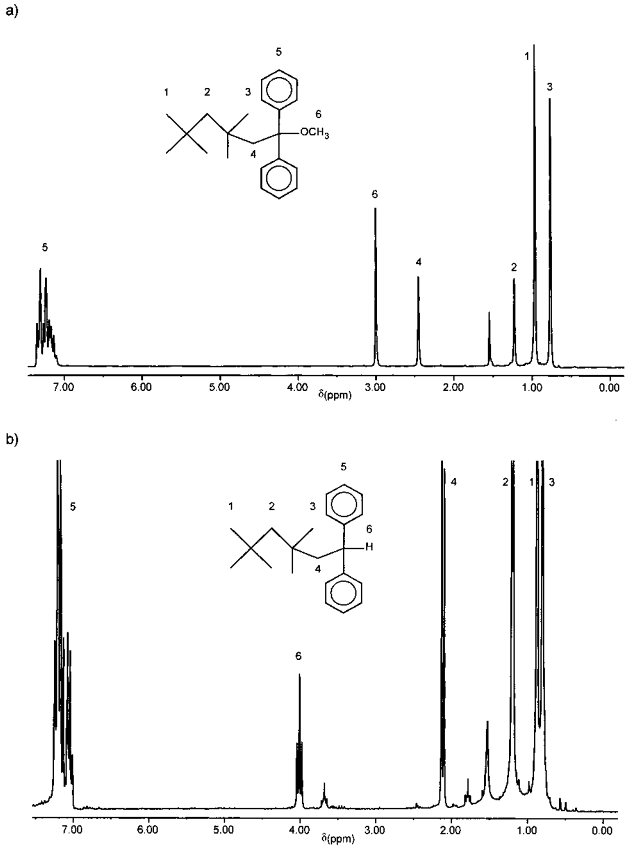


Figure 2. ^{1}H NMR spectra (200 MHz in CDCl$_3$) of **2** (a) and the metalated product after quenching with methanol (b) (reaction time for metalation with K/Na alloy, 30 min). The signal at 1.55 ppm is due to water in CDCl$_3$.

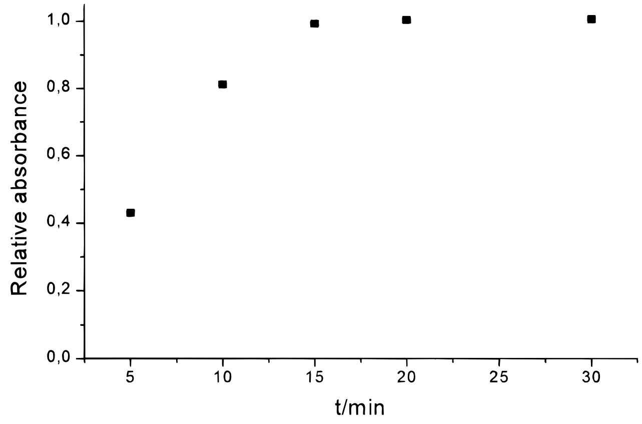


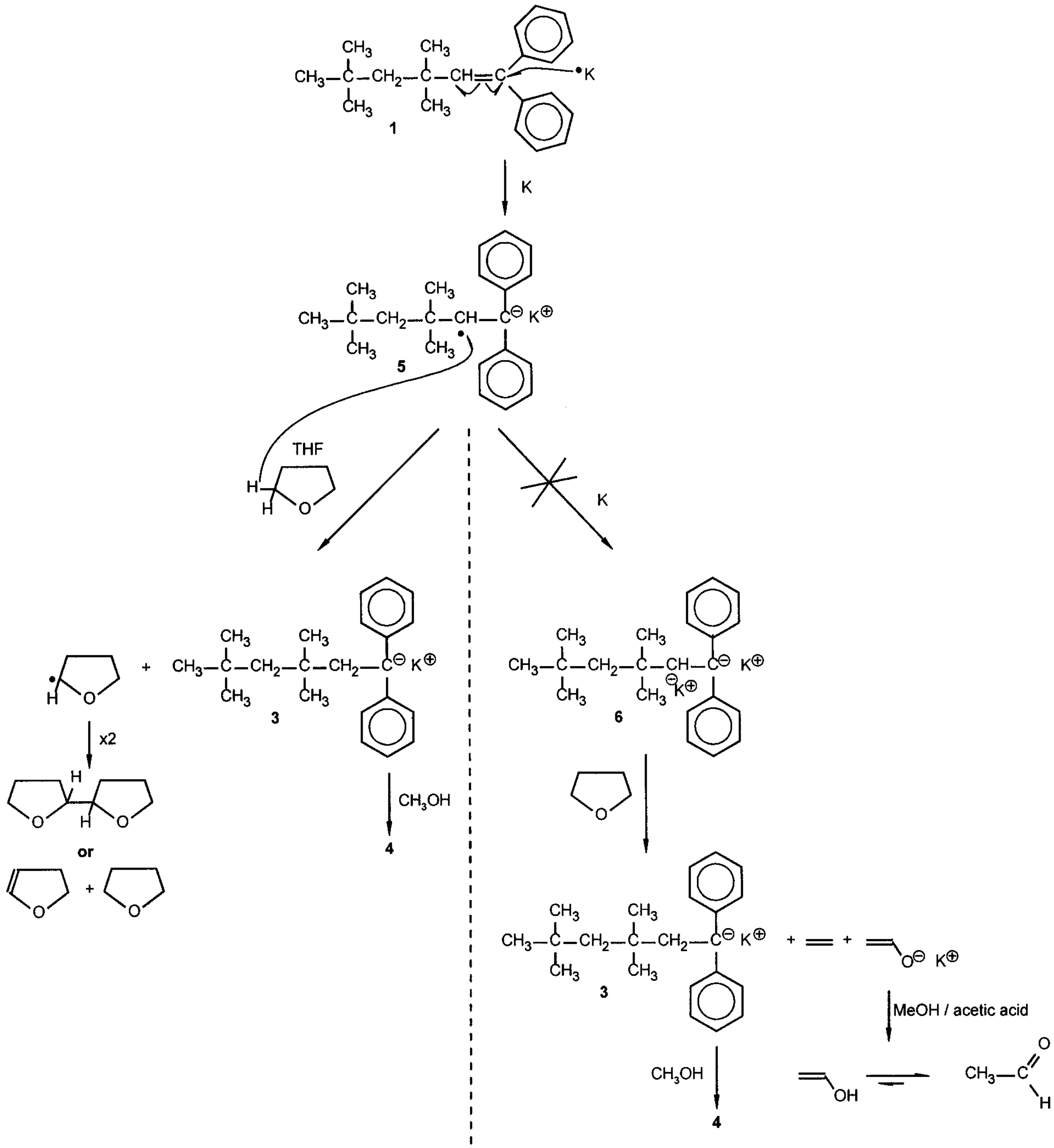
Figure 3. Relative UV absorbance at $\lambda_{max} = 480$ nm as a function of time during metalation of **1** with potassium/sodium alloy (■).

tetramethyl-1,1-diphenylhex-1-ene (**1**) or 1-methoxy-3,3,5,5-tetramethyl-1,1-diphenylhexane (**2**) are the products of this process as shown in Scheme 1.

Converting these cationically obtained compounds to stable carbanions suitable to initiate living anionic polymerization was attempted in the course of our studies. It was found that quantitative lithiation of **1** with a variety of lithiating agents, e.g., alkyllithiums, cannot be achieved, most likely due to steric hindrance.[17] Therefore, our attention has turned toward direct metalation reactions leading to diphenyl-stabilized carbanions. It was reported by Ziegler and coworkwers[19,20] that certain ethers, such as 1-methoxy-1,1-diphenylethane and 2-methoxy-2-propylbenzene (CumOMe), can be metalated by potassium. However, the yields of such ether cleavage reactions either were not determined or were found less than quantitative with the examined compounds and by the applied methods. Recently, even an improved metalation of CumOMe with K/Na alloy led only to 85% conversion[21] most likely because this reaction is not free from side reactions, such as coupling and dianion formation.

As outlined in Scheme 2, K/Na alloy, Cs metal, or Li dispersion were selected for carrying out ether cleavage of **2** in our studies. The reaction mixture becomes dark red characteristic for the diphenyl-substituted carbanion **3** right after the addition of a THF solution of **2** to a K/Na suspension in THF. The extent of the metalation

Scheme 3. Metalation of 1



reaction was followed by UV−visible and ^{1}H NMR spectroscopies. The UV−visible spectrum of the THF solution of the formed carbanion **3** has an absorption maximum at $\lambda = 480$ nm. As Figure 1 shows, the relative absorbance at this wavelength reaches a constant value after about 30 min with K/Na and 45 min in the presence of Cs. Metalation with lithium (30% (w/w) lithium dispersion in mineral oil, containing <0.05% Na) is about 100 times slower than with K/Na or Cs. In the latter case the consistency of the Li dispersion might have some influence on the rate of metalation. $\lambda_{max} = 502$ nm for the lithium compound is somewhat higher than that for K or Cs (both about 480 nm), and it is in good agreement with $\lambda_{max} = 496$ nm observed for 1,1-diphenylhexyllithium.[22] The resulting carbanionic species exhibit high stability as indicated by the fact that the value of the absorption does not change even after storing the solutions under inert atmosphere for more than 10 days.

Quenching the carbanionic system with methanol leads to the hydrogenated product, 3,3,5,5-tetramethyl-1,1-diphenylhexane (**4**). This reaction was used to determine the yield of the metalation reaction. As shown in Figure 2, the characteristic signal for the methyl protons of the methoxy group completely disappears after reacting **2** with K/Na for 30 min, and a proton signal at 4.0 ppm (triplet) appears after quenching with methanol. Integrals are in agreement with the given structures. These data indicate that the metalation reaction is quantitative leading to carbanion **3**. This finding also proves that the constant relative absorption value of the UV−visible spectra after a certain reaction time corresponds to quantitative metalation.

Metalation of DPE leads to the formation of a radical anion which subsequently couples, resulting in a dianion.[23] Metalation of **1** with K/Na alloy was also attempted. As shown in Figure 3, this reaction also leads

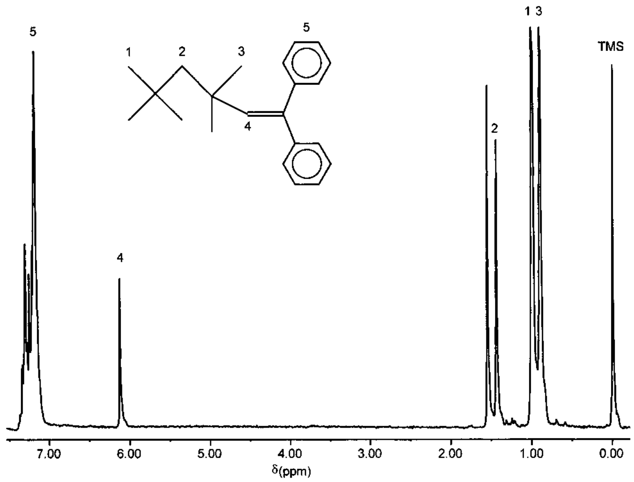


Figure 4. ^{1}H NMR spectrum (200 MHz in CDCl$_3$) of **1**. The signal at 1.55 ppm is due to water in CDCl$_3$.

to quantitative metalation. It exhibits the relative absorbance of the formed carbanion indicating quantitative reaction within 15 min. Figure 4 shows the ^{1}H NMR spectra of the starting compound, **1**. The ^{1}H NMR spectrum of the product formed by quenching the carbanionic system with methanol is identical to the one in Figure 2b. Complete disappearance of the vinyl proton signal at 6.12 ppm is evidence for quantitative metalation. Surprisingly, no coupling could be detected by ^{1}H NMR. The integration ratio of the signals at 2.15 and 4.0 ppm is 2:1 as expected. In the case of coupling, the signal at 2.15 ppm would change from a doublet to a triplet. The UV−visible spectrum of the resulting product was identical with that of the carbanion formed by reacting **2** with K/Na or Cs. Both carbanions have an absorption maximum at $\lambda = 480$ nm. Further evidence verifying this postulate is given later together with the polymerization results.

We assume that the metalation reaction of **1** with K/Na alloy in THF occurs by formation of a radical anion **5** in the first step as shown in Scheme 3. Most probably **5** quickly abstracts a hydrogen atom from the solvent THF leading to the stable carbanion **3**. THF radicals easily disappear by recombination or disproportionation. An alternative possibility is the reaction between the radical anion **5** with a second K atom leading to an instable dianion **6**. This yields **3** by abstracting a proton from THF, and the cyclic anion will decompose to ethylene and vinyl alcoholate (acetaldehyde enolate). In order to test whether acetaldehyde is present or not, metalation with K/Na alloy was performed in THF-d_8. After the reaction was quenched with methanol and acetic acid, the crude product was analyzed by ^{1}H NMR. Not even traces of aldehyde protons in the range 9−10 ppm could be detected. Gas chromatography measurements also indicate the absence of acetaldehyde. On the basis of these results we assume that the metalation proceeds by the mechanism mentioned first.

These new quantitative metalation reactions have great synthetic significance. The product formed quantitatively between a carbocationic species and DPE can be a mixture of DPV- and MDPE-containing compounds depending on reaction conditions.[17] Since the metalation of both groups leads to the same carbanion quantitatively, converting such cationically obtained products to diphenyl-stabilized carbanionic species is not sensitive at all to the composition of the mixture containing **1** and **2**.

Table 1. Precursor, Initial Concentrations of Initiator, [I]$_0$, and Monomer, Yield, Number Average Molecular Weight, M_n, Polydispersity Index, M_w/M_n, and Initiating Efficiency, *f*, in Polymerization of Methyl Methacrylate (MMA) by Lithiated 1 and 2

precursor	10^3[I]$_0$, M	[MMA], M	yield, %	$10^{-3}M_n$ (SEC)	M_w/M_n (SEC)	f [a]
1	2.29	0.35	100	16.2	1.04	1.04
2	6.16	0.32	100	5.5	1.09	1.00
2	4.00	0.26	100	6.6	1.07	0.97

[a] $f = M_{n,theo}/M_{n,exp}$, where $M_{n,theo}$ is calculated from the molar ratio of monomer and initiator used in each experiment.

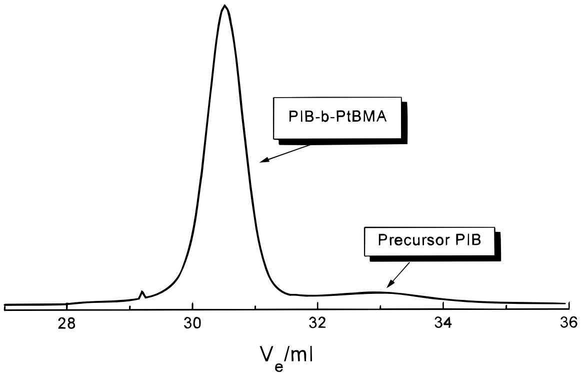


Figure 5. SEC eluogram (UV, 260 nm) of PIB-*b*-PtBMA block copolymer.

The formation of **3** was also proved by using this stable carbanion for the initiation of living anionic polymerization of methyl methacrylate (MMA). After K$^+$ with Li$^+$ were replaced by adding excess LiCl, the initiating ability of the resulting anions was tested by charging MMA. The results of these polymerization experiments are shown in Table 1. As these data indicate, metalation of either **1** or **2** followed by replacement of K$^+$ with Li$^+$ yields new anionic initiators with quantitative initiating efficiencies leading to PMMA with desired M_n and narrow molecular weight distribution. These findings directly prove that the metalation of **1** and **2** with K/Na alloy or Cs metal is quantitative and leads to stable carbanions capable of initiating living anionic polymerizations. On the basis of these results coupling of **5** to form a dianion can be excluded too, since this should result in doubling of the molecular weight and an apparent initiating efficiency, $f = 0.5$.

In order to demonstrate the application of the above-mentioned procedure for the synthesis of block copolymers, an example involving a polyisobutylene (PIB) precursor ($M_n = 6000$) is given. In Figure 5 an SEC eluogram of an AB block copolymer, polyisobutylene-*b*-poly(*tert*-butyl methacrylate) (PIB-*b*-PtBMA) is shown (crude product before precipitation). By integration of the respective UV signals (260 nm) corresponding to the precursor and the block copolymer, a blocking efficiency of >95% could be determined.

On the basis of these results, not only a large variety of new low molecular weight materials but new types of polymeric architectures can be synthesized with macroinitiators obtained by metalation of compounds or polymers containing DPV and/or MDPE end groups. Details concerning the synthesis and characterization of AB and ABA block copolymers will be reported in a subsequent publication.[24]

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