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Notes

(9-Anthracenylmethyl)lithium-Initiated Living Anionic Polymerization of Alkyl Methacrylates

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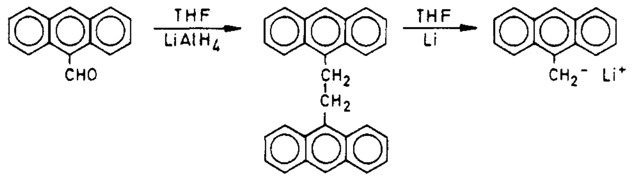
Polymers bearing luminescent labels are becoming increasingly important tools in the study of microenvironmental phenomena.[1-5] Conventional ways for introducing luminescent labels are mainly based on copolymerization of labeled monomers[6] or modification of a preformed polymer,[7] while deactivation of a living polymer by a label-containing substrate has also been studied extensively.[8] The former two methods suffer from a poor control of the chromophore content and especially of the chromophore distribution within the polymer chains. The latter method is also exposed to limitations, due to the possible limited efficiency of the living chain deactivation process. In contrast to the previous methods, a truly living polymerization initiated with a label-containing species should give rise to a polymer, one chain end of which is capped by one chromophore.

Let us recall that 9-anthracenylmethyl carbanion has been known for some time[7] as a reagent able to introduce 9-anthracenylmethyl pendant groups by nucleophilic substitution of appropriate monomer units.[9] To our best knowledge this labeled carbanion has never been considered as a possible initiator in anionic polymerization.

This note aims at reporting preliminary results using (9-anthracenylmethyl)lithium as a highly efficient initiator for the living anionic polymerization of methyl methacrylate in THF at -78 °C.

As schematized hereafter, (9-anthracenylmethyl)lithium was synthesized by metalation of a suspension of 1,2-di-9-anthracenylethane by lithium metal in THF.[7,9] 1,2-Di-9-anthracenylethane was prepared by reduction of 9-anthraldehyde with $LiAlH_4$ in THF (Scheme I), previously distilled from sodium–benzophenone (mp 315 °C).

Scheme I



Anionic polymerizations were carried out in carefully dried laboratory glassware under a high-purity nitrogen atmosphere. THF was distilled from sodium–benzophenone. Methyl methacrylate was first distilled from calcium hydride and, just before use, from triethylaluminium in order to remove the last traces of protic impurities.[11] Predetermined quantities of initiator were added with a syringe through a septum-fitted stopcock to the THF-containing polymerization reactor. After cooling to -78 °C, the intense green color of the 9-anthracenylmethyl carbanion solution changed immediately to a faint yellow upon addition of the appropriate amount of methyl methacrylate. Figure 1 illustrates that the experimental molecular weights [$\overline{M}_n$(exptl)] of poly(methyl methacrylate) samples, as determined by GPC, closely match the theoretical value based on the molar ratio of the monomer over the (9-anthracenylmethyl)lithium initiator. In addition, molecular weight distributions are narrow (Table I), monomodal (Figure 2), and comparable with those obtained by using other efficient initiators of the anionic polymerization of methacrylates, such as (diphenylhexyl)lithium or (α-methylstyryl)lithium.[11] The polymer yield is quantitative. This new initiator opens the way to the synthesis of homopolymers and random and block polymers of various alkyl methacrylates bearing only one chromophore per chain. The selective labeling technique reported in this paper provides for the direct determination of $\overline{M}_n$ by simply using Beer's law. Figure 3 shows indeed the linear inverse dependence of the number average molecular weight of poly(methyl methacrylate) versus the relative absorbance of the labeled end groups at 369 nm in THF. Figure 4 illustrates the absorption spectrum of the 9-anthracenylmethyl-terminated poly(methyl methacrylate) of 54 000 $\overline{M}_n$ in THF.

With respect to absorbance measurements of the 9-anthracenylmethyl-labeled polymers as compared to the absorbance of the model compound 9-methylanthracene, the end group analysis by UV spectroscopy suggests a smaller value than 1 9-anthracenylmethyl group/polymer chain on average, approximately 0.8 9-anthracenylmethyl group/chain. This same observation

Table I
Characteristic Data for the Anionic Polymerization of Methyl Methacrylate in THF at -78 °C, Initiated by (9-Anthracenylmethyl)lithium

cf	9-AMeLi, mol × 10^{-4}	MMA, g	MMA, mol	$\overline{M}_n$(theor)[b]	$\overline{M}_n$(exptl)[a]	$\overline{M}_w$(exptl)[a]	$\overline{M}_w/\overline{M}_n$
L1	6.3	15.2	0.15	24 100	29 000	34 000	1.17
L2	4.5	12.0	0.12	26 800	33 000	38 000	1.15
L3	2.8	13.0	0.13	46 400	52 000	62 000	1.19
L4	2.0	11.0	0.11	54 500	54 000	61 000	1.13
L5	2.5	19.6	0.20	78 500	82 000	96 000	1.17
L6	1.7	14.2	0.14	85 600	94 000	109 000	1.16

[a] GPC data were obtained on a Waters 200 instrument in THF at 35 °C using a PMMA calibration curve. [b] Calculated from the monomer to initiator molar ratio.

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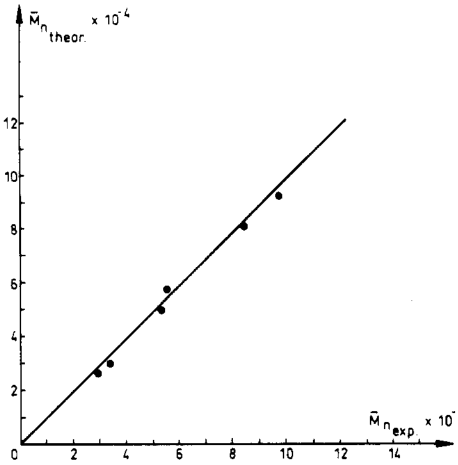

Figure 1. Plot of calculated $\overline{M}_n$ versus experimental values obtained from GPC measurements for the anionic polymerization of methyl methacrylate in THF at −78 °C initiated by (9-anthracenylmethyl)lithium.

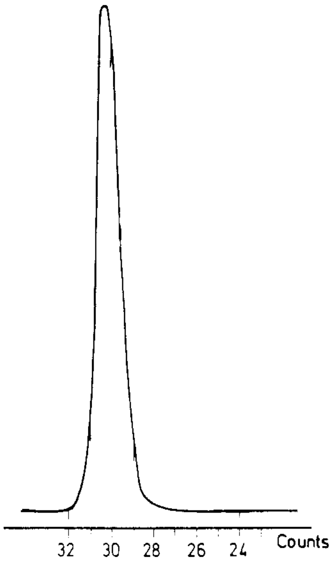

Figure 2. GPC chromatogram of α-9-anthracenylmethyl poly(methyl methacrylate).

was made for poly(methyl methacrylate), synthesized by initiation with the reaction product of butyllithium with 1-α-naphthyl-1-phenylethylene. For these end-labeled polymers as well, UV spectroscopy gave a too low value of naphthalene end groups per chain using the molar absorption coefficient of 1-naphthylmethyl pivalate as a model compound.[12] Thus end-group analysis of labeled polymers by UV spectroscopy should be subject to careful examination.

In this way, (9-anthracenylmethyl)lithium extends the rather limited number of highly efficient and easily handled initiators for the living anionic polymerization of alkyl methacrylates, resulting in quantitative polymer yield and molecular weights as predicted by the monomer over initiator molar ratio. In addition, this new initiator provides for a selective 9-anthracenylmethyl labeling process of linear poly(alkyl methacrylates). Extension of that technique to the anionic polymerization of various monomers is under way as well as the synthesis and characterization of fluorescent α-labeled amphiphilic block copolymers. These results will be the subject of future publications.

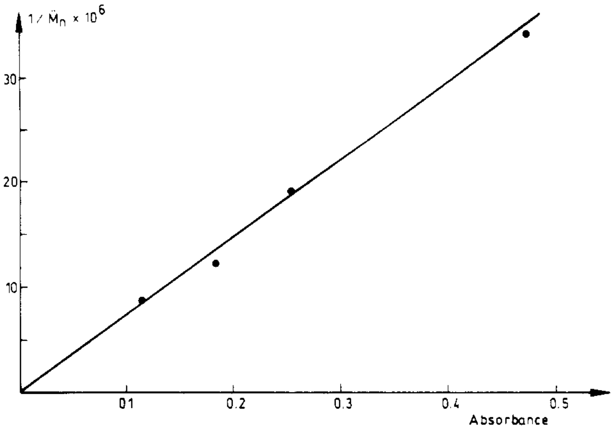

Figure 3. Plot of the inverse linear dependence of the $\overline{M}_n$ of α-9-anthracenylmethyl poly(methyl methacrylate) versus absorbance (concn of polymer in THF 0.17 g dL^{-1}).

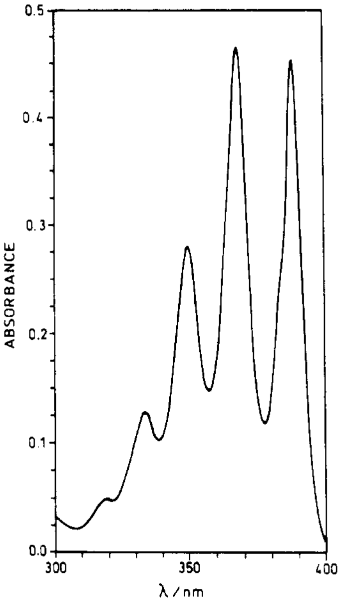

Figure 4. Absorption spectrum of α-9-anthracenylmethyl poly(methyl methacrylate) in THF ($\overline{M}_n$ = 54 000; concn of polymer in THF 0.38 g dL^{-1}.

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Registry No. (9-Anthracenylmethyl)lithium, 88920-43-8; poly(methyl methacrylate), 9011-14-7.