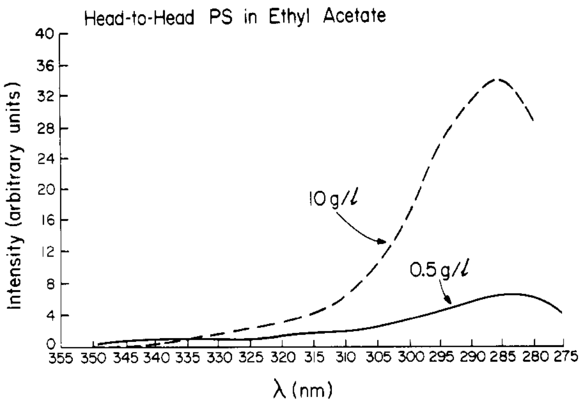

Figure 3. Fluorescence spectra of head-to-head polystyrene in ethyl acetate.

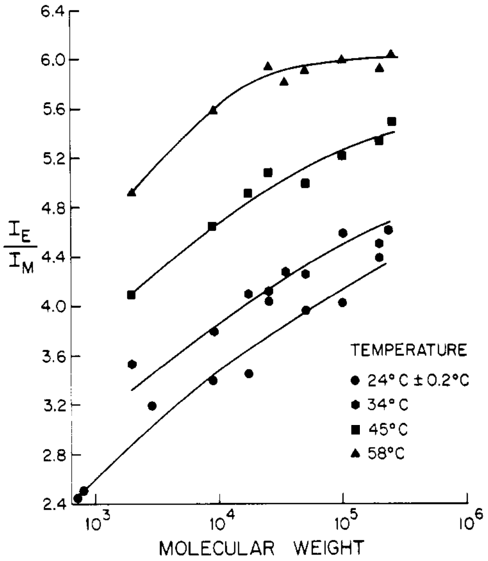

Figure 4. Effect of temperature on the molecular weight dependence of I_E/I_M for polystyrene in cyclohexane.

perature, and the data suggest a plateau I_E/I_M at high temperature, similar to that found in the room-temperature study in dichloroethane. Although we cannot yet explain the reasons for the molecular weight effect in poor solvents, we can conclude that the effect is due to solvent quality and not to other properties peculiar to a single solvent.

Finally, we note that a paper by Lindsell et al.[27] appeared during the preparation of this paper which studied the spectrum of head-to-head polystyrene more extensively. They reach the same conclusion about the dominance of nearest-neighbor excimers as we have based upon different evidence. Our present observation of the persistent molecular weight dependence of I_E/I_M remains to be explained.

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High-Performance Liquid Chromatography Analysis of Polymers. Separation of Hydroxy-Functional Poly(methyl methacrylate) by Number of Hydroxyls and Separation of Poly(methyl methacrylate) Oligomers

We have found that high-performance liquid chromatography (HPLC) is an excellent method for separation of hydroxy-functional methacrylate polymers. Narrow molecular weight distribution, hydroxy-functional poly(methyl methacrylate) (PMMA) made by anionic polymerization can be separated by HPLC into fractions based on the number of hydroxyl groups per molecule. Additionally, HPLC can be used to separate not only individual oligomers of PMMA but also different diastereomers of each oligomer.

Terminal hydroxy-functional PMMA **2** was prepared by hydrolysis of the acetal-terminal PMMA **1**.[1] Functional

$$\underset{\mathbf{1}}{\mathrm{EtOCH(CH_3)O(CH_2)_4CPh_2(MMA)_nH}} \rightarrow \underset{\mathbf{2}}{\mathrm{HO(CH_2)_4CPh_2(MMA)_nH}}$$

polymers such as **2** are typically analyzed for functionality by some sort of hydroxyl equivalent analysis.[2] Hydroxyl equivalent weights consistent with projected and measured values of M_n are judged to prove that each polymer molecule contains a hydroxyl group.

A more convincing structure proof for these methacrylate polymers follows from the chromatographic be-

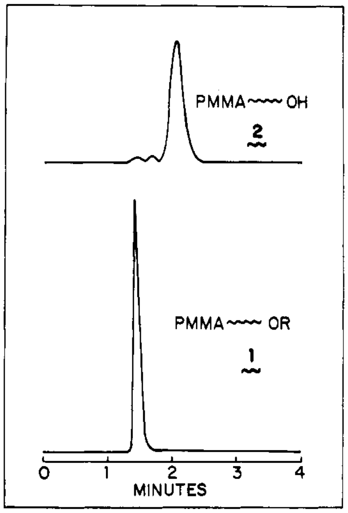


Figure 1. HPLC of acetal- and hydroxy-ended PMMA on a 250 × 3.2 mm silica gel (5-μm particles, 6-nm pores) column with ethyl acetate eluent at 1.0 mL/min; UV detector at 254 nm.

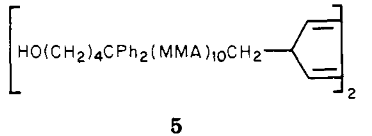
havior of 1 and 2. On a silica gel HPLC column with ethyl acetate eluent, 1 (n = 10) elutes as a single peak at the solvent front (Figure 1). Ethyl acetate is polar enough to overcome adsorption of the PMMA ester groups onto the silica gel. The polar hydroxyl group of 2 (n = 10), however, interacts strongly with the silica gel and causes the material to be retained on the column (Figure 1). The p-nitrobenzoate ester of 2 behaves chromatographically like 1, demonstrating that the hydroxyl group is responsible for the success of the separation. The eluted peaks are narrow because the polymers are nearly monodisperse ($M_w/M_n \sim 1.1$); broader distribution samples give broader peaks. When a silica gel column with pores large enough (10 nm) to eliminate size-exclusion effects is used, hydroxy-PMMA 2 with M_n to 10 000 ($n \simeq 100$) can be separated with nearly base line resolution from its acetal precursor 1. This simple and rapid analysis provides direct proof that nearly every polymer molecule contains one hydroxyl group. Classical functional group analysis only shows that there is an average of one hydroxyl group per molecule.

A similar analysis can be used to verify the functionality of polymers with other functional groups. The allyl-ended PMMA 3 was prepared by capping (1,1-diphenylhexyl)lithium-initiated PMMA with allyl bromide.[1] It was converted to hydroxy-terminal PMMA 4 by hydroboration

$$\underset{3}{C_5H_{11}CPh_2(MMA)_{20}CH_2CH{=}CH_2} \rightarrow \underset{4}{C_5H_{11}CPh_2(MMA)_{20}(CH_2)_3OH}$$

with 9-borabicyclo[3.3.1]nonane followed by oxidation with hydrogen peroxide.[3] Polymers 3 and 4 were separated by HPLC in the same manner as 1 and 2 to show that the capping reaction with allyl bromide (and the hydroboration reaction) proceeded in at least 95% yield.

The living PMMA precursor to 1 was coupled with 1,4-bis(bromomethyl)benzene to give dihydroxy-PMMA 5.[1] The coupling yield in the reaction producing 5 is



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lowered by deviations from the required stoichiometry of the reactants and by reactions which deactivate the living polymer. The yield can be estimated by comparison of M_1, the M_n of precursor polymer, and M_2, the M_n of the coupled polymer, by the formula % yield = $200(1 - M_1/M_2)$. The errors inherent in the usual methods of determining M_n of these polymers make this estimate of coupling yield inaccurate, especially when small amounts of the monofunctional material are to be measured.

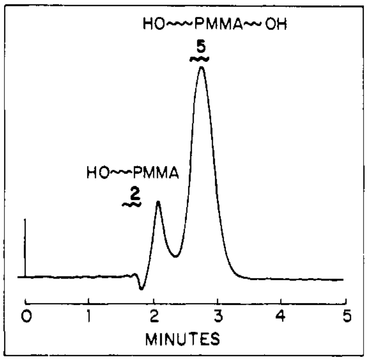


Figure 2. HPLC separation of monohydroxy- and dihydroxy-PMMA with the same conditions as Figure 1 and refractive index detection.

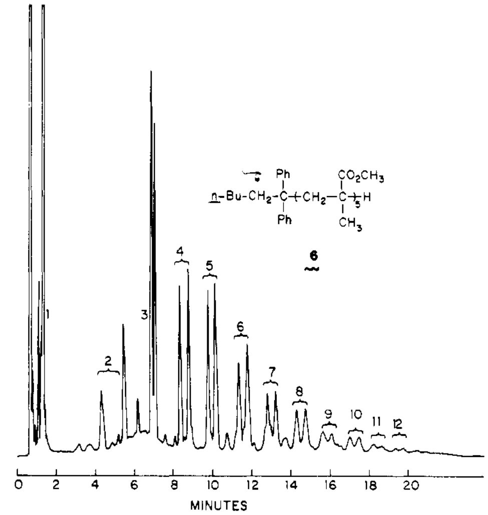


Figure 3. HPLC separation of hydrogen-capped PMMA oligomers on the same column as in Figure 1. Conditions: gradient elution of 1% acetonitrile/butyl chloride to 20% acetonitrile in 20 min, UV detector at 254 nm.

The same HPLC separation serves to differentiate the dihydroxy polymer 5 from 2 and other monohydroxy materials with end groups other than hydrogen which are produced as byproducts in the coupling reaction (Figure 2). The extra hydroxyl group of 5 causes it to be more strongly retained on the column than 2. Samples of the two peaks shown in Figure 2 were isolated by preparative HPLC. GPC molecular weight determination showed that the peak assigned as the difunctional polymer 5 has a number-average molecular weight twice that of the monofunctional material. The HPLC analysis provides both a method for structure proof for the polymers and a simple, rapid analytical method for monitoring the effects of different reaction conditions. We have extended this method to the analysis of the products of coupling living PMMA with 1,2,4,5-tetrakis(bromomethyl)benzene. Fractions with 1, 2, 3, and 4 hydroxyl groups were isolated in pure form and their molecular weights were verified by GPC analysis.

Separations of polymers by end group have been done with very nonpolar polymers such as polybutadiene by thin-layer chromatography (TLC), but little of the details have been published.[4] Polystyrene capped with sugar residues (hydroxyl groups), from grafting onto cellulose,

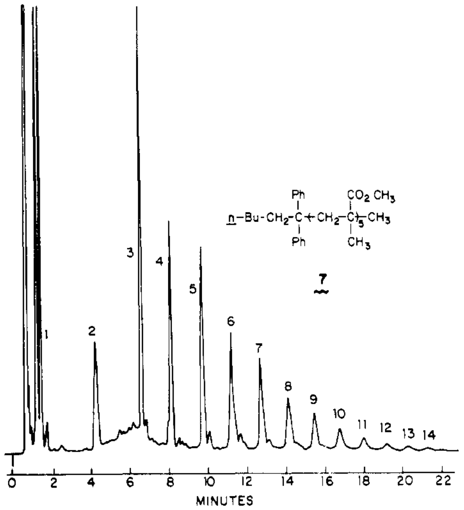
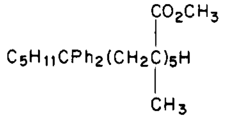


Figure 4. HPLC separation of methyl-capped PMMA oligomers under the same conditions as Figure 3.

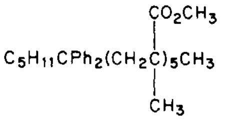
has been separated from homopolystyrene by TLC.[5] An elegant separation of poly(styrene)carboxylic acid from polystyrene by TLC and column chromatography has been reported.[6] Our studies show that the separations are general and can be used with polar polymers.

That such narrow peaks are observed for these polymers is remarkable because a polymer of DP = 10, prepared by anionic polymerization, has significant amounts of oligomers from DP = 3 to DP = 18.[7] Also, a polymer such as PMMA has 2^{n-1} possible diastereomers for each oligomer of DP = n (512 for DP = 10). A solvent of sufficient polarity to overcome the adsorption of the ester groups onto the silica gel must be used to obtain narrow peaks. When a solvent less polar than ethyl acetate is used, the peaks become broader because of the adsorption of the ester groups. If a sufficiently nonpolar solvent is used, individual oligomers of the PMMA can be separated. Figure 3 shows a separation of PMMA **6**, prepared by initiation of MMA polymerization with (diphenylhexyl)lithium.[1]

Analysis of individual components of **6**, purified by


$C_5H_{11}CPh_2(CH_2\overset{CO_2CH_3}{\underset{CH_3}{C}})_5H$

6


$C_5H_{11}CPh_2(CH_2\overset{CO_2CH_3}{\underset{CH_3}{C}})_5CH_3$

7

preparative HPLC, verified the molecular compositions of the oligomers with DP = 1–3. The presence of two major peaks per chain length suggested that separation by the relative stereochemistry of the last two methacrylate units occurs. This was confirmed by the observation that for PMMA **7**, which lacks the terminal asymmetric center present in **6**, only one major peak is observed for each chain length (Figure 4). There are many reports of HPLC separations of oligomers in the literature, but none of oligomers with the stereochemical complexity of PMMA.[8]

HPLC has great potential utility for the analysis of polymers. The examples here demonstrate this for some highly structured polymers made by anionic polymerization. In the future we will report on the use of HPLC to analyze both simple and complex polymers such as polyethers and polyesters.

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Chain Motion in the Amorphous Regions of Polyethylene As Revealed by Deuteron Magnetic Resonance

The renewed discussion about the nature of molecular motion and glass transition in polyethylene[1,2] prompts us to give a preliminary report of a detailed study employing ^{2}H NMR. Deuterons offer unique possibilities for studying molecular motions:

i. The NMR parameters of ^{2}H with spin $I = 1$ are almost exclusively governed by the quadrupole interaction[3] which originates from the electrons in the C–H bond. Thus ^{2}H NMR yields direct information about rotational motions involving the C–H bond direction.[4,5]

ii. The ^{2}H NMR line shapes can quantitatively be analyzed to discriminate between different types of motion.[5,6] Since the rigid solid spectrum spans a frequency range of approximately 250 kHz, the line shape will only be affected by motions with spectral densities extending above 10^6 Hz.

iii. The standard spin relaxation times[3] T_1 and T_2 yield information about the spectral densities of the motion at the NMR frequency ($\sim 10^8$ Hz) and at low frequencies ($\sim 10^4$ Hz), respectively. The latter value is determined by the natural line width of ^{2}H NMR lines due to the dipolar coupling between the deuterons. This limitation has recently been overcome by the creation of deuteron spin alignment, offering the possibility of extending the accessible range down to frequencies as low as 10–100 Hz as in case of mobile deuterons in polyethylene.[7]

iv. Over the temperature range studied (125–390 K) the ^{2}H spin–lattice relaxation time, T_1, in the mobile amorphous regions is shorter by at least a factor of 50 than T_1 in the crystalline regions. This can be exploited to separate the respective contributions to the NMR signal. Thus, all the spectra presented here correspond essentially to the mobile deuterons, the rigid ones being largely saturated.

In this communication, we present some preliminary results of applying these ^{2}H NMR techniques to polyethylene. We have investigated a sample of perdeuterated linear polyethylene (LPE) ($M_w \approx 100\,000$, $M_w/M_n \approx 10$, Merck, Darmstadt) that was isothermally crystallized from the melt at 396 K. The ^{2}H spectra shown in Figures 1 and 2 originate essentially from deuterons in the amorphous regions: In the temperature region ($\sim$230–380 K) where the line shape of the mobile deuterons is motionally narrowed, their contribution to the *total* intensity of ^{2}H NMR signals amounts to about 29%, to be compared with an amorphous fraction of 26% as determined by X-rays.[4]