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Polymers with controlled degradability through end-modification of poly(α-methylstyrene) derivatives

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The end-modification reactions of poly(α-methylstyrene) (PMS) derivatives were examined as a means of inducing degradabilities in polymers in response to environmental conditions. When diphenylphosphine chloride was used as a modifier for the living end of *para*-substituted PMS, the coupling efficiency was ~ 50%. 2-Phenylallyl halide derivatives such as 2-phenylallyl bromide, 2-(4-tolyl)allyl bromide and α-trifluoromethylstyrene were found to be suitable end-modification agents. For example, ω-2-phenylallyl PMS was prepared with almost quantitative functionality by the reaction of the living PMS with 2-phenylallyl bromide. In a similar way, ω-3,3-difluoro-2-phenylallyl and ω-2-(4-tolyl)allyl PMS derivatives were synthesized. On the basis of thermogravimetric analysis, onset of the degradation temperature of the end-modified PMS derivatives decreased in the following order: ω-hydrogen- > ω-3,3-difluoro-2-phenylallyl- > ω-2-phenylallyl- > ω-2-(4-tolyl)allyl-PMS. The onset temperature of ω-2-(4-tolyl)allyl-PMS derivatives was in fact 50°C lower than that of ω-H-PMS derivatives. These results indicate that the active species is produced effectively at the end unsaturated bond, which initiates the depolymerization of the polymer at fairly low temperatures. Ionic degradation of these polymers was also investigated using butyllithium as an anionic initiator and methanesulfonic acid as a cationic initiator. Tendencies similar to the thermal degradation were observed. Therefore, it is concluded that a 2-phenylallyl substituent at the end of the PMS chain induces effective degradation through several mechanisms such as radical, anionic and cationic depolymerization reactions. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(α-methylstyrene); end-modification; degradable polymer; thermal degradation; ionic degradation)

INTRODUCTION

Environmental pollution by a large amount of undecomposable waste has recently become a serious problem. Therefore biodegradable polymers, which can be degraded by environmental species such as bacteria and enzymes, have been extensively studied[1]. Most of the biodegradable polymers prepared so far have been polyester derivatives such as poly(hydroxybutyrate/valerate)[1–4], poly(lactide)[5] and poly(glycolide)[6]. The degradation mechanism is the hydrolysis of the ester groups in the main chain of the polymer, which is facilitated by enzyme degradation.

Most of the mass-produced polymers, however, are vinyl-polymerized plastics such as poly(ethylene), poly(propylene) and poly(styrene). There is no technology for the degradation of such vinyl polymers except in the lithography field, in which it is known that some vinyl polymers can be used for posi-type resists by decomposition with u.v. or electron-beam (e.b.)[7].

For creation of degradable polymers, the following three factors must be considered seriously: (i) What degrades the polymer? (ii) For how long does the polymer maintain its initial properties? (time history of the mechanical strength, etc.) and (iii) Bioactivity of the liberated oligomers. The aim of our work is the creation of new polymers in which the above three factors can be easily controlled.

Ito and his coworkers pointed out that poly(α-methylstyrene), which had been synthesized by cationic polymerization was easier to depolymerize by acid treatment than that obtained by other polymerization techniques[8]. They explained that the easier depolymerization tendency of cationically synthesized poly(α-methylstyrene)s was due to the end double bond formed by the proton transfer reaction in the cationic polymerization process. However, the extent of the double bonds at the end of the polymer chain should not be quantitative in the cationic polymerization process. Our idea was to synthesize depolymerizable polymers possessing a functional end group quantitatively, which can initiate depolymerization from the end group of the polymer in response to certain stimuli.

If we can degrade polymers from the end of the polymer chain, two advantages ensue: (i) we can control several properties of the polymers undergoing degradation by choosing the degradation source (pH, light, u.v., e.b., etc.) and control the rate of degradation by changing the structure of the end group; (ii) production of oligomers, which may induce a significant problem in

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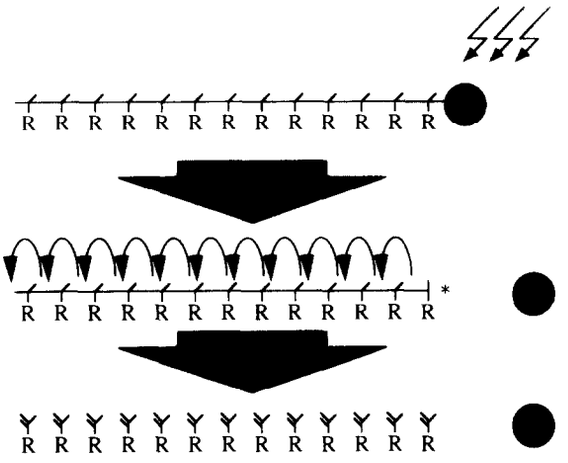


Scheme 1

terms of bioactivity, can be suppressed because of depolymerization from the end of the polymer (only the monomer will be liberated). In this paper, we describe the results of the end functionalizations of poly(α-methylstyrene) derivatives and their degradation characteristics under various temperature, acid and alkaline conditions.

EXPERIMENTS

Materials

Commerical THF (Wako) was purified by the following method. The THF was pre-dried with KOH for several days, then the reflux was carried out over lithium aluminium hydride for 5 h, followed by distillation. The fraction at 68°C was collected and stored under Ar atmosphere. sec-Butyllithium (sec-BuLi, Aldrich, in cyclohexane) was used as received, its concentration being determined by a gas chromatography (g.c.) technique; i.e., sec-BuLi was reacted with 1,1-diphenylethylene (DPE), then the unreacted DPE was quantified by g.c. Commercial α-methylstyrene (MS, Wako) and chlorodiphenylphosphine (CDP, Wako) were dried over calcium hydride and purified by fractional distillation under reduced pressure. 4-[Bis(trimethylsilyl)methyl]isopropenylbenzene (SMS) was synthesized according to our previous paper[9]. Purification of SMS was carried out by the same method as MS. 2-Phenylallyl bromide (PAB)[10], 2-(4-tolyl)allyl bromide (TAB) and α-trifluoromethylstyrene (FMS)[11] were prepared according to the literature; in the case of TAB, the same procedure as in reference 10 was employed, using 4-isopropenyltoluene as the starting material. Other materials were used as received.

Polymerization procedure

A typical anionic polymerization was performed in a 100 ml round-bottomed flask with a 3-way stopcock. The reactor was first carefully washed with a hexane solution of butyllithium, following which THF (6.6 ml), SMS (3.1 g, 10 mmol) and sec-butyllithium (0.28 ml, 0.50 mmol, 1.77 mol l^{-1}) were added via a syringe at −78°C. The colour of the mixture immediately turned brownish red. The reaction was allowed to continue for 20 min.

For an end-modification reaction, a 2–5 times excess molar amount of an end coupling agent such as CDP, PAB, TAB and FMS was added to the living polymer solution and allowed to react for a further 20 min. The resulting mixture was analysed by gel permeation chromatography (g.p.c.) and then poured into a large excess methanol. The precipitate was purified by 3-fold successive reprecipitation from THF solution. The polymer obtained was freeze-dried with benzene to remove the solvents employed.

Degradation experiments

Acid degradation was investigated as follows. Methanesulfonic acid (0.1 ml) was added to a toluene solution (1 ml) of the polymer sample (60 mg) and stirred for 30 min. After neutralization by pyridine, the mixture was analysed by g.p.c. For basic degradation, 0.2 ml of n-BuLi was added to a THF (1 ml) solution of the polymer sample (70 mg) and stirred for 1 h. The mixture was analysed by g.p.c.

Analysis

Thin layer chromatography (t.l.c.) was carried out by silica-gel (WAKO-70FM plate) using hexane or hexane/CCl_4 as eluent. A Hewlett-Packard 5890 Series II GC was used (column: glass capillary column DB-1 0.25 mm $\phi \times$ 30 m). G.p.c. measurements were performed on a Shimadzu LC 6A liquid chromatograph with an RID-6A i.r. detector and TSK-gel G4000H8 + G3000H8 + G2500H8 columns. ^{1}H and ^{13}C n.m.r. spectra (^{1}H: 399.65 MHz; ^{13}C: 100.53 MHz) were measured on a JEOL EX400 spectrometer using $CDCl_3$ as a solvent at room temperature. Chemical shifts relative to $CHCl_3$ (^{1}H: $\delta = 7.26$) and $CDCl_3$ (^{13}C: $\delta = 77.0$) were employed. Thermogravimetric analysis (t.g.a.) was carried out on a Mettler TA 4000 scanning calorimeter.

RESULTS AND DISCUSSION

Preparation of end-functionalized poly(α-methylstyrene) derivatives

Following the procedure described in the experimental section, the living polySMS was prepared in THF at −78°C. It is well known that living polymers having a molecular weight larger than a few ten thousands can be obtained under appropriate conditions, especially in the case of anionic polymerization of styrene and α-methylstyrene. In this study, however, we prepared polymers having a molecular weight in the range 1000–5000, to facilitate the end group analysis. When CDP was added to the living polymer solution the dark red colour of the solution disappeared immediately, suggesting that the living end reacted with the CDP. The number average molecular weight of the polymer was 3400 with a polydispersity (M_w/M_n) of 1.14 as determined by g.p.c. As shown in *Figure 1*, however, the polymer thus obtained was separated in two spots by t.l.c. One of the spots corresponding to $R_f = 0.84$ was very close to a hydrogen-terminated polymer ($R_f = 0.82$), indicating that the polymer obtained was a mixture of diphenylphosphine-terminated and hydrogen-terminated polymers. Based on the ratio of the area of the two spots, the efficiency of the end modification was 52%.

There have been several reports on the coupling reaction of living anionic polymers with halogenated compounds. Not only alkyl halides[12] but also metal

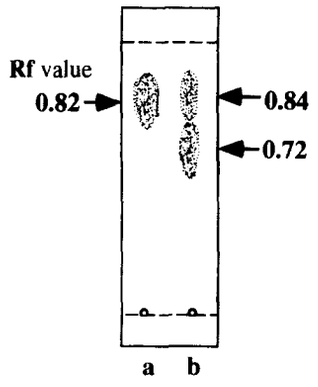


Figure 1 Thin layer chromatograms of polySMS terminated by methanol (a) and by CDP (b) (eluent = hexane)

halides such as silyl chloride[13] can be utilized for the coupling reaction with high coupling efficiency under appropriate conditions. In the case of phosphine chloride, however, some undesired side reactions such as a lithium–proton exchange reaction between the living polymer and CDP and a cleavage reaction of the preformed C–P bond by the living polymer may take place during the coupling reaction. This may be one of the reasons for the low coupling efficiency with CDP.

Otsu and his coworkers reported the introduction of a 2-methoxycarbonylallyl group at the end of the PMMA chain by radical telomerization reactions, using 2-methoxycarbonylallyl bromide as a telogen[14]. In the case of anionic polymerizations, alkyl halides cannot be utilized as chain transfer agents because of the lack of ability of the liberated lithium halide to initiate the reaction. Therefore, an alkyl halide can only be used as the coupling agent for the living end after almost all monomers have been consumed. Because PAB, TAB and FMS possess both carbon–halogen and carbon–carbon double bonds in the same molecule, there are several possibilities in the reaction with the carbanion. If both functions react with the living end carbanions, several side reactions such as dimerization of the prepolymers and oligomerization of the coupling agent with the prepolymers can take place. *Figure 2* shows the g.p.c. trace of the polySMS treated with PAB. The M_n of the polymer was 4700 with a fairly narrow *MWD* (1.11), indicating no possible side reactions. From t.l.c. analysis, as shown in *Figure 3*, the end-functionalized polymer appeared at $R_f = 0.63$ though a slightly hydrogen-terminated polymer was detected at $R_f = 0.80$. Introduction of the double bond at the polymer end was confirmed by ^{1}H n.m.r. analysis; viz., the two singlet signals appearing at 4.5 and 4.9 ppm were assignable to two olefinic protons at the end of the polymer, while the signal appearing at 0.4 ppm originated from methyl protons in the sec-butyl group at the α-end originating from the initiator[15]. The ratio of olefinic protons to methyl protons was 2/6, indicating an almost quantitative introduction of the double bond at the ω-end. The molecular weight of the polymer, determined from ^{1}H n.m.r. using the olefinic protons and aromatic protons (6–7.4 ppm) was 5400, which agreed well with that from g.p.c., which also supports the almost quantitative end-functionalization efficiency.

Ito and his coworkers investigated the reaction of FMS with small molecular weight alkyllithium

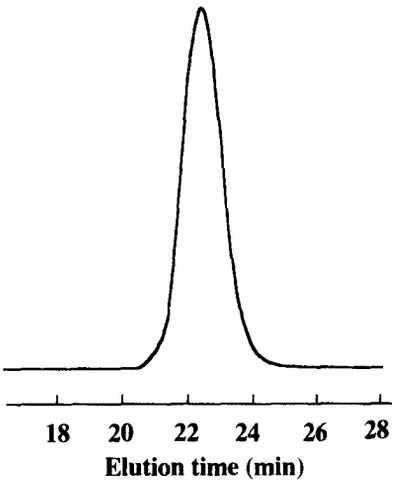


Figure 2 G.p.c. trace of polySMS terminated by PAB (same sample as run 4 in *Table 1*)

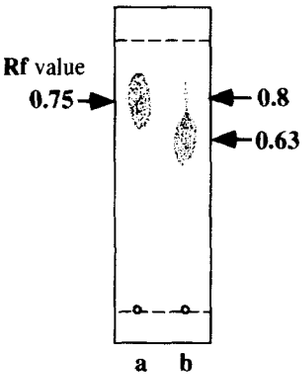
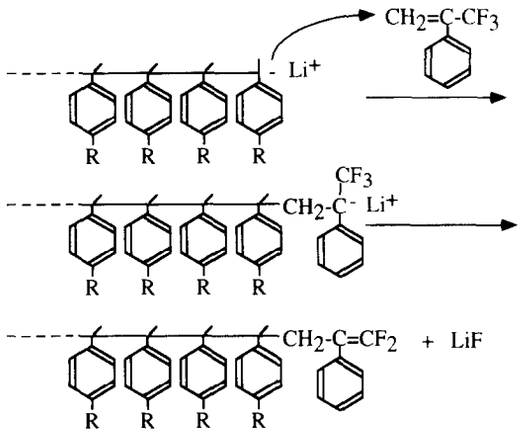


Figure 3 Thin layer chromatograms of polySMS terminated by methanol (a) and by PAB (b) (eluent = hexane/CCl_4 = 75/25 vol.%)

compounds and found that alkyllithium reacted with FMS in several complicated ways other than a simple coupling reaction[16]. We investigated the reaction of FMS with alkyllithium at the end of the PMS chain. The g.p.c. of the polymer, obtained from the coupling reaction with FMS, showed a unimodal peak with a narrow *MWD* ($M_n = 1500$; $M_w/M_n = 1.10$), indicating that a possible coupling reaction between two (or more) polymer molecules with FMS can be excluded, probably because of the high molecular weight of the prepolymer lithium. The ω-end group of the polymer was analysed on the basis of the ^{13}C n.m.r. spectra[15]. In the case of the ω-hydrogen-terminated polymer, the C^1 signal at the ω-end appeared at 152 ppm, while the signal at 152 ppm disappeared completely in the FMS-treated polymer, indicating the complete derivatization of the polymer end. Instead of the signal assignable to the ω-hydrogen-terminated C^1 carbon, several new signals appeared in the FMS-terminated polymer. The signal appearing at 135 ppm can be assignable to the ω-C^1-carbon in the 3,3-difluoro-2-phenylallyl end group. The triad signal at 154 ppm and that at 91 ppm were assignable respectively to $C=\underline{C}F_2$ and $\underline{C}=CF_2$ at the ω-end. From these results, it is concluded that the FMS-treated polymer has a 3,3-difluoro-2-phenylallyl group quantitatively at the ω-end of the polymer. Almost the same intensity of the α-terminal C^1 signal appearing at 143 ppm as the ω-terminal one at 135 ppm supported the above

conclusion. The 3,3-difluoro-2-phenylallyl group was considered to be introduced at the ω-chain end as follows: the carbanion adds to the double bond of the FMS molecule, followed by the elimination of LiF as shown in *Scheme 2*.

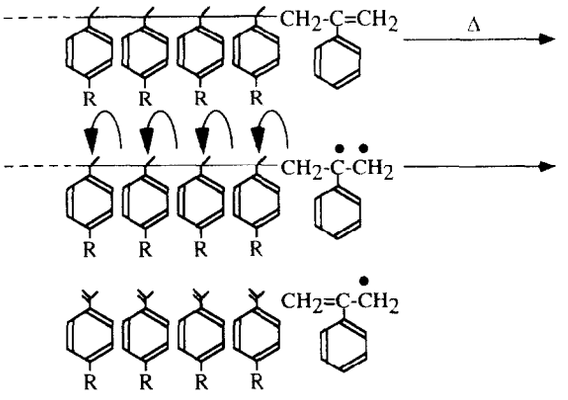


Scheme 2

When TAB was used as the coupling agent, a reaction similar to that with PAB proceeded quantitatively. On the basis of these results, the terminal double bond can be introduced at the ω-end of the living poly(α-methylstyrene) derivatives using 2-phenylallyl halide derivatives such as PAB, TAB and FMS. *Table 1* summarizes the end-functionalized poly(α-methylstyrene) derivatives synthesized using these techniques.

Degradation behaviour of the end-functionalized poly(α-methylstyrene)s

The degradation behaviour of the end-functionalized poly(α-methylstyrene) derivatives was investigated. The thermal degradability of these polymers was investigated by thermogravimetric analysis (t.g.a.). The hydrogen-terminated polySMS started to degrade at 340°C, as shown in *Figure 4*. Then the 2-phenylallyl group was introduced at the end of the polymer chain, the onset temperature of degradation was lowered. This can be explained as follows: the high temperature induced the cleavage reaction of the end-double bond to form a radical species, which initiated the depolymerization reaction of the poly(α-methylstyrene) derivatives as shown in *Scheme 3*.



Scheme 3

The onset temperature of degradation was controlled by the substituent in the 2-phenylallyl-end group. When fluorine atoms were introduced to the double bond the onset temperature was raised, indicating that the electron-withdrawing character of the fluorine atoms makes the active species stabler than that of the repeating units. On the other hand, the polymer started to degrade at a fairly low temperature when a methyl group was introduced at the *para*-position of the benzene ring in the 2-phenylallyl end group. It is considered that the electron-donating character of the *para* methyl group makes initiation easier. On the basis of these results, it is concluded that the introduction of a 2-phenylallyl group at the chain end of poly(α-methylstyrene) derivatives is

Table 1 Results of the end-functionalization of living poly(α-methylstyrene) derivatives[a]

Run	Monomer	$[Monomer]_0$ (mmol)	$[sec\text{-}BuLi]_0$ (mmol)	End-modifier	$[End\text{-}modifier]_0$ (mmol)	$M_n \times 10^3$ Calc.	$M_n \times 10^3$ G.p.c.	$M_n \times 10^3$ n.m.r.	M_w/M_n G.p.c.	Functionality (%)
1	SMS	10	0.6	MeOH	–	4.7	5.0	–	1.06	0
2	SMS	10	0.6	CDP	6.0	4.9	4.6	n.d.	1.07	52[b]
3	SMS	5	1.4	PAB	4.1	1.0	1.9	2.1	1.07	85[c]
4	SMS	5	0.28	PAB	2.1	5.0	4.7	5.4	1.11	101[c]
5	SMS	10	0.6	PAB	2.0	4.8	4.8	n.d.	1.06	n.d.
6	SMS	10	0.6	TAB	2.0	4.8	4.9	n.d.	1.05	n.d.
7	SMS	5	0.8	FMS	1.6	1.8	1.5	2.6	1.10	n.d.
8	SMS	7	0.4	FMS	0.4	4.9	4.3	6.3	1.09	100[b]
9	MS	20	0.5	MeOH	–	4.8	5.1	n.d.	1.05	0
10	MS	20	0.5	PAB	2.0	4.9	4.6	4.8	1.05	96[d]
11	MS	20	0.5	TAB	2.0	4.9	4.8	n.d.	1.05	n.d.
12	MS	20	0.5	FMS	2.0	4.9	5.4	n.d.	1.06	

[a] $[Monomer]_0 = 1.0\,mol\,l^{-1}$; solvent, THF; temp., −78°C; polymerization time, 20 min; end-modification time, 20 min
[b] Determined by t.l.c.
[c] Determined by ^1H n.m.r. using signals of α-sec-butyl and ω-olefinic protons
[d] Determined by ^1H n.m.r. using signals of ω-olefinic protons and phenyl protons in the repeating units

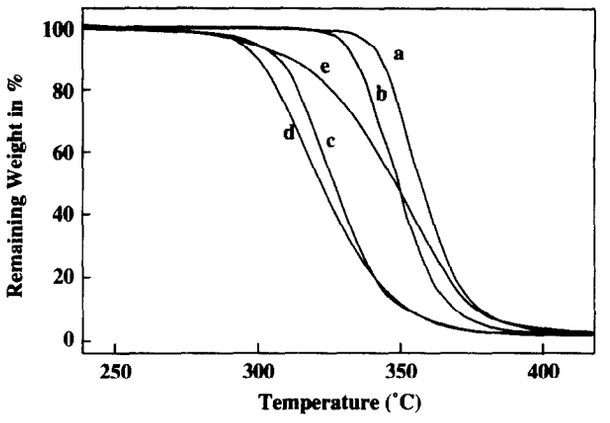
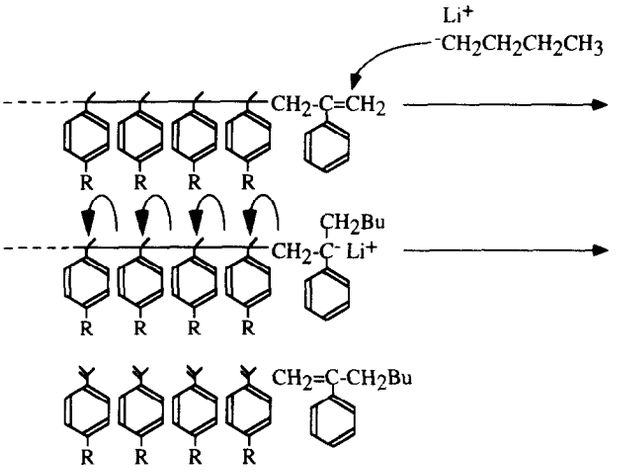


Figure 4 T.g.a. profiles of poly(α-methylstyrene) derivatives. End group: H (a); 3,3-difluoro-2-phenylallyl (b); 2-phenylallyl (c); 2-(4-tolyl)allyl (d); and diphenylphosphine (50%) (e). (Temperature range, 30–500°C; rate 20°C min^{-1}; under Ar atmosphere)

one of the suitable methods for the preparation of polymers degradable by the radical mechanism.

In the case of a diphenylphosphine-terminated polymer, the polymer started to degrade at a fairly low temperature. However, the temperature for complete degradation of the polymer was the same as that of the hydrogen-terminated polymer. This fact indicates that the end C-$P(Ph)_2$ bond is effective for production of the active species. However, the low degree of substitution (52% in this case) requires a wide range of degradation temperature.

Acceleration of the degradation was also shown in the reaction with a strong base. *Figure 5* shows g.p.c. traces of the end-functionalized polySMS after treatment with n-BuLi. When the 2-phenylallyl-terminated polySMS was mixed with n-BuLi in THF at ambient temperature, almost all of the polymer disappeared (*Figure 5c*). A low molecular weight oligomeric mixture was observed instead of the starting polymer. This is in sharp contrast to the hydrogen-terminated polymers, which remained almost completely intact after the reaction with n-BuLi (*Figure 5a*). The 2-(4-tolyl)allyl-ended polySMS also shows the same tendency as that of the 2-phenylallyl-ended polymer (*Figure 5d*). These results indicate that butyllithium adds to the double bond at the end of the polymer chain to form the active carbanion, followed by depolymerization reactions as shown in *Scheme 4*.



Scheme 4

When a fluorine-containing polymer was treated with n-BuLi, almost no degradation occurred. In this case, some undesirable reactions such as coupling and exchange reactions between BuLi and the fluoroolefin at the end of the polymer chain may take place.

The acid-catalysed depolymerization was also effective for the 2-phenylallyl-terminated poly(α-methylstyrene) derivatives. When the hydrogen-terminated polySMS was treated with methanesulfonic acid in hexane at ambient temperature for 30 min, almost no degradation took place (*Figure 6a*), whereas 2-phenylallyl-terminated polySMS was degraded by methanesulfonic acid treatment under the same conditions (*Figure 6c*). The

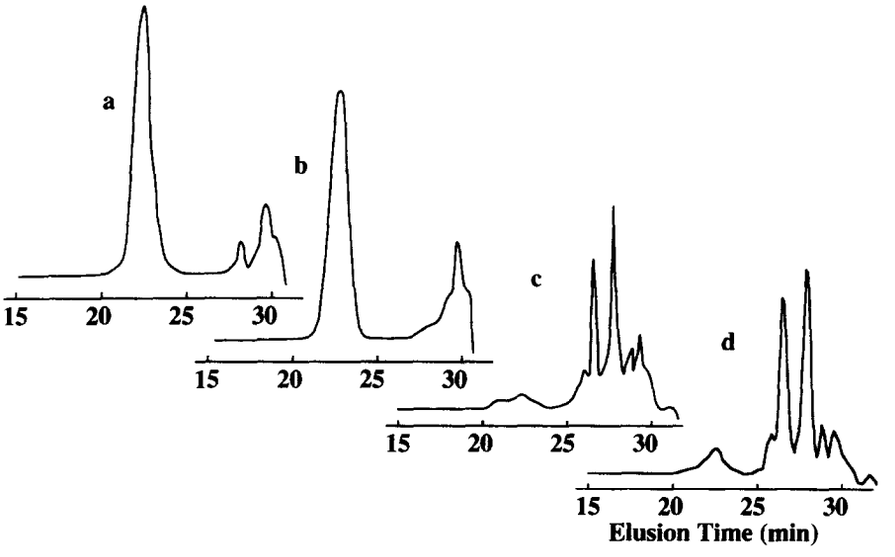


Figure 5 G.p.c. traces of reaction mixture of polySMS derivatives with n-BuLi in THF at room temperature for 1 h. End group: H (a); 3,3-difluoro-2-phenylallyl (b); 2-phenylallyl (c); and 2-(4-tolyl)allyl (d)

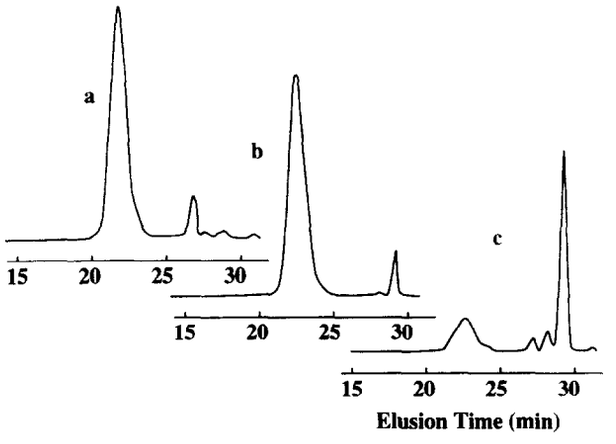


Figure 6 G.p.c. traces of reaction mixture of polySMS derivatives with methanesulfonic acid in hexane at room temperature for 30 min. End group: H (a); 3,3-difluoro-2-phenylallyl (b); and 2-phenylallyl (c)

3,3-difluoro-2-phenylallyl-terminated polymer was again not so sensitive to acid treatment. This can be explained by the low reactivity of the fluorine-containing double bond toward methanesulfonic acid, i.e. the difficulty of producing active species at the end of the polymer chain because of the electron-withdrawing effect of fluorine atoms.

CONCLUSION

End-modification reactions of living anionic poly(α-methylstyrene)s were carried out. When 2-phenylallyl halide was used as the end modifier, the modification efficiency was attained almost quantitatively. The 2-phenylallyl-terminated polymer was degraded more easily than the hydrogen-terminated polymer by radical, anionic and cationic mechanisms. The degradation was controlled by the substituent in the 2-phenylallyl group at the end of the polymer chain.

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