Anionic polymerization of t-butyl methacrylate using a new type of bifunctional initiator

Koji Ishizu*
Department of Polymer Science, Tokyo Institute of Technology, 2-12 Ookayama, Meguro-ku, Tokyo 152, Japan

and Yoshiharu Kondo and Mikio Takaki
Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan
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The living character of the anionic polymerization of t-butyl methacrylate (BMA) using 2,3-diphenylbutadienemagnesium (DPB–Mg) as a bifunctional initiator was investigated by varying the polymerization conditions. Anionic polymerization of BMA at both −78 and −45°C involved no transfer reaction and the molecular weight distribution of poly(t-butyl methacrylate) was very narrow ($\bar{M}_w/\bar{M}_n = 1.20$). However, the polymerization at 0°C involved a small amount of side reaction, i.e. attack of the living ends of the ester molecules. The structure of the DPB–Mg complex was characterized by spectroscopic analysis and quantitative titration of Mg metal.

(Keywords: living character; anionic polymerization; t-butyl methacrylate)

INTRODUCTION

Most of the vinyl monomers having polar substituents participate in various side reactions with anionic initiators. The one group of polar vinyl monomers which has been most extensively investigated is the acrylates, especially methyl methacrylate (MMA). It has been shown[1,2] that organolithium compounds, besides initiating polymerization through the vinyl groups, also react substantially with the carbonyl function. With n-butyllithium (n-BuLi) in toluene at 30°C, about 60% of the initiator disappears by this side reaction, while 1,1-diphenylhexyllithium[3,4] and 1,1-diphenyl-3-methylpentyllithium[5] undergo none of this side reaction. It was found also from our results[6] that sodium triphenylmethane is one of the most useful initiators for living polymerizations of methacrylic monomers. On the other hand, inorganic and organometallic additives such as alkali metal and alkaline-earth metal salts and metal alkyls and alkoxides have been shown to form complexes with the active species that could prevent disturbance of the course of the anionic polymerization by secondary transfer and termination reactions[7]. It has been shown recently that the use of μ-coordinating salts such as LiCl is an efficient way of avoiding side reactions that are normally associated with the true anionic polymerization of alkyl methacrylates and t-butyl acrylate when carried out at low temperature[8,9].

The polymerization of methacrylic monomers by anionic initiators such as Grignard reagents often involves many active species with different reactivities and stereospecificities. Hatada *et al.*[10,11] found that t-C_4H_9MgBr prepared in diethyl ether caused no side reaction in the polymerization of MMA in toluene and formed pure poly(methyl methacrylate) (PMMA) with a narrow molecular weight distribution. Polymerizations of MMA by n-, iso-, and s-C_4H_9MgBr were also investigated in toluene. As a result, with an increase in bulkiness of the alkyl group the isotacticity of the polymer increased and the molecular weight distribution became narrower. More recently, Kondo and coworkers[12] have synthesized 2,3-diphenylbutadienemagnesium (DPB–Mg) and investigated the possibility of using this compound as a bifunctional anionic initiator in the anionic polymerization of a few monomers, such as styrene and 2-vinylpyridine.

In the work described in this article, we studied the living character of an anionic polymerization of t-butyl methacrylate (BMA) initiated by DPB–Mg under various polymerization conditions. The structure of DPB–Mg was characterized by spectroscopic analysis and quantitative titration of Mg metal.

EXPERIMENTAL

Synthesis of 2,3-diphenylbutadienemagnesium

2,3-Diphenyl-1,3-butadiene (DPB) was synthesized by Grignard's method[13] involving the reaction of the

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* To whom correspondence should be addressed

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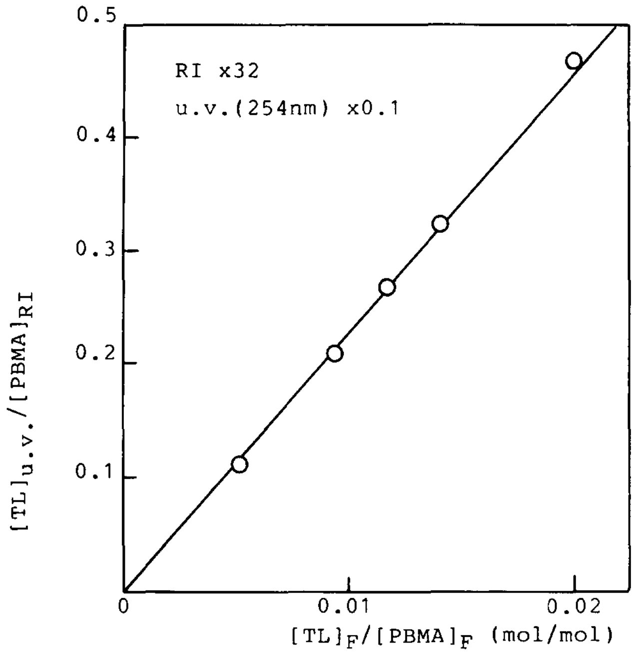


Figure 1 Calibration curve constructed from a mixture of PBMA and toluene (TL) using g.p.c. double detectors (*RI* and u.v. at 254 nm): $[TL]_{u.v.}$, area of g.p.c. distribution of toluene in u.v. monitor (254 nm); $[PBMA]_{RI}$, area of g.p.c. distribution of PBMA in *RI* monitor; $[TL]_F$, feed (mol) of toluene in the mixture; $[PBMA]_F$, feed (mol) of PBMA in the mixture

Grignard reagent of α-bromostyrene with acetophenone. The DPB–Mg complex was synthesized by the Grignard reaction of DPB with magnesium ribbon in tetrahydrofuran (THF) at room temperature under high vacuum. This solution was characteristically red ($\lambda_{max}=378$ nm, $\varepsilon_{max}=1.06\times10^4$ l mol^{-1} cm^{-1}).

Polymer synthesis and characterization

PBMAs were prepared by the usual anionic technique. BMA monomer was dried over calcium hydride and purified with n-BuLi *in vacuo*. THF was distilled under vacuum from its solution of sodium/α-methylstyrene. The anionic polymerization was carried out in a sealed glass apparatus under a pressure of 10^{-6} mmHg using the break seal method. Anionic polymerization of BMA was carried out in the range of temperature from −78 to 0°C and at concentrations below 8 wt%. After the polymerization, the ends of the PBMA anions were protonated using methanol. The polymerization product was purified twice by reprecipitation from a THF solution with methanol/water (7/3 v/v).

The number-average molecular weight ($\bar{M}_n$) of PBMA was determined by gel permeation chromatography (g.p.c.; Tosoh high-speed liquid chromatograph HLC-8020) with THF as eluent at 38°C, a TSK gel GMH_{XL} column and a flow rate of 1.0 ml min^{-1}, with the aid of universal calibration[14]. The molecular weight distribution ($\bar{M}_w/\bar{M}_n$) was determined from g.p.c. distribution functions improved by the reshaping method[15] with a personal computer. The number of central phenyl groups in the PBMA (corresponding to initiator fragments) was determined from the area ratio of the refractive index (*RI*) and u.v. (254 nm) intensities on a g.p.c. chart (using a calibration curve constructed from a mixture of PBMA homopolymer and toluene (*Figure 1*), where this homopolymer was synthesized by anionic polymerization of BMA initiated by n-BuLi in THF at −78°C and terminated with methanol).

Scission of initiator fragment in PBMA

In order to check the anionic propagation from two active species of DPB–Mg, we carried out the scission reaction of the central double bonds of the initiator fragments in the PBMAs by two methods. One method was ozonolysis of the double bond of the butadiene unit. Cleavage of the double bond was performed at 25°C over 20 min by dissolving PBMA in chloroform (0.1 wt%) containing a 40-fold excess of ozone to butadiene units[16]. After the chloroform had been evaporated the resulting polymer was precipitated from THF with a methanol/water mixture. It is well known that 1,2-diphenylethylene is scarcely cleaved by ozone and the double bond is instead converted to epoxy groups due to the resonance of the double bond with the phenyl groups[17]. Other workers have studied the cleavage of styrene–butadiene rubber[18] and natural rubber[19]. The action of peroxybenzoic acid on natural rubber yielded a product containing adjacent hydroxy groups. Materials with this structure could be cleaved by periodic acid, a specific 1,2-glycol splitting agent, to yield degradation products with aldehyde or carboxy groups. So, we also tried the scission reaction of PBMA by this method. The epoxidation of PBMA was carried out at room temperature over 24 h in benzene containing a 10-fold excess of peroxybenzoic acid to butadiene units. The benzene was evaporated and the resulting polymer was precipitated from THF with a methanol/water mixture. Subsequently, this polymer was cleaved by periodic acid in dioxane/water (7/3 v/v) at 70°C over 5 h. The polymer after ozonolysis was also cleaved by periodic acid.

The second method was the scission of double bonds using an alkali metal. Poly(2,3-diphenylbutadiene) is easily cleaved by an alkali metal reagent such as sodium naphthalenide[20]. So, PBMA was dissolved in THF and reacted with sodium naphthalenide at −78°C for 48 h. The mixture gradually changed from green to purple. The resulting polymer was precipitated with a methanol/water mixture. The g.p.c. distributions of the PBMAs before and after scission reactions were taken with *RI* and u.v. double monitors. The reductions in molecular weight and phenyl group content were also derived.

Structure of DPB–Mg initiator

An aliquot of DPB–Mg initiator solution was taken and the THF solvent was distilled to another ampoule at liquid nitrogen temperature under high vacuum; the ampoule containing the DPB–Mg residue was removed from the apparatus. The C_6D_6 solution of the DPB–Mg complex was prepared in an n.m.r. tube under high vacuum. The structure of the DPB–Mg complex was studied by ^{1}H n.m.r. (270 MHz, JEOL GX 270 n.m.r. spectrometer). The Mg content of the DPB–Mg complex was determined by a chelatometric titration using ethylenediaminetetraacetic acid (EDTA).

RESULTS AND DISCUSSION

A solution of the DPB–Mg complex goes from red to yellow (characteristic colour of the PBMA anion) after addition of BMA monomer. A yellow solution of PBMA

Table 1 Anionic polymerization of BMA at 0°C[a]

Experiment number	Feed ($\mathrm{mol\,l^{-1}}$) $10^4[\mathrm{I}]_0$	$10^2[\mathrm{M}]_0$	Time (h)	Conversion (%)	$10^{-4}\bar{M}_n$ ($\mathrm{g\,mol^{-1}}$)	$\bar{M}_w/\bar{M}_n$
P11	1.284	3.16	0.75	95.9	5.8	1.38
P12	1.284	3.16	2.0	99.8	6.4	1.39
P13	1.284	3.16	5.5	100	6.6	1.39

[a] Polymerized in THF (80 ml)

Table 2 Anionic polymerization of BMA at −78°C[a]

Experiment number	Feed ($\mathrm{mol\,l^{-1}}$) $10^4[\mathrm{I}]_0$	$10^2[\mathrm{M}]_0$	Time (h)	Conversion (%)	$10^{-4}\bar{M}_n$ ($\mathrm{g\,mol^{-1}}$)	$\bar{M}_w/\bar{M}_n$
P21	1.212	3.11	3	10.0	1.5	1.19
P22	1.212	3.11	18	20.8	2.4	1.19
P23	1.212	3.11	25	31.8	3.1	1.20
P24	1.212	3.11	50	46.0	3.7	1.20

[a] Polymerized in THF (80 ml)

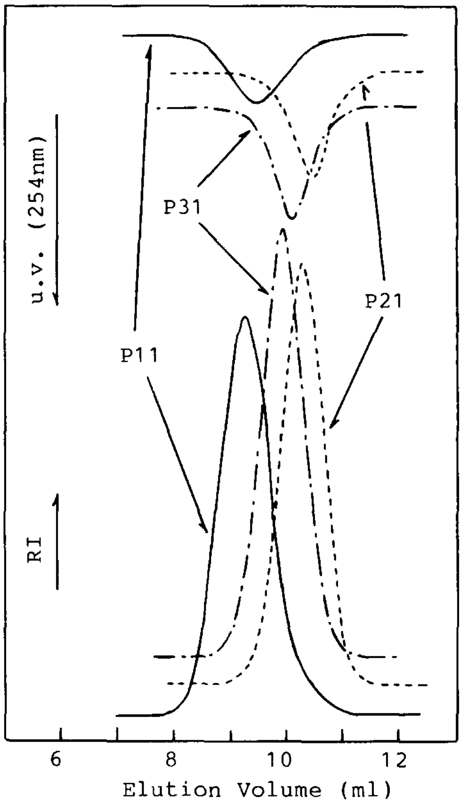


Figure 2 G.p.c. profiles of P11, P21 and P31 taken with *RI* and u.v. (254 nm) monitors

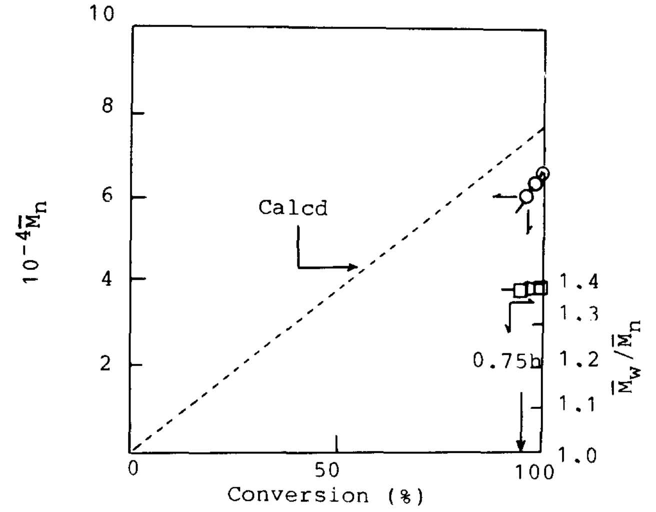


Figure 3 Plots of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ against conversion for the P11–P13 series

anion becomes colourless in the termination process upon addition of methanol. *Table 1* lists the anionic polymerization conditions and results for BMA at 0°C (P11–P13). The monomer conversion reached 96% after 0.75 h and BMA monomer was consumed almost completely within 2 h. A typical g.p.c. profile of P11 is shown in *Figure 2*. The g.p.c. profiles of P11–P13 were unimodal. The molecular weight distributions of these products were not so narrow ($\bar{M}_w/\bar{M}_n = ca$ 1.40). The number of phenyl groups in P11 was *ca* 2.0 per molecule from the g.p.c. distribution measured with *RI* and u.v. double detectors. *Figure 3* shows the plots of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ against conversion for the P11–P13 series. The dashed line represents the calculated $\bar{M}_n$ values assuming that one polymer forms by propagation from the bifunctional DPB–Mg initiator (degree of polymerization $\overline{DP} = 2[\mathrm{M}]_0/[\mathrm{I}]_0$). Although the observed $\bar{M}_n$ values increase with monomer conversion, these values come below the dashed line. These results suggest that the anionic polymerization of BMA at 0°C proceeds with no termination but with a small amount of transfer. Under these polymerization conditions, the mechanism involves not only rapid initiation but rapid propagation. However, growing active chain ends attack the ester groups competitively.

Next, we carried out the anionic polymerization of BMA at −78°C (P21–P24, see *Table 2*). Under these conditions, the monomer conversion is extremely low (10%) after 3 h and reaches only 46% after 50 h. A typical g.p.c. profile of P21 is shown in *Figure 2*; its distribution pattern is unimodal. Products P21–P24 have narrower molecular weight distributions ($\bar{M}_w/\bar{M}_n = ca$ 1.20) than the P11–P13 series. The number of phenyl groups in each of P21–P24 was close to 2.0 per molecule as determined by g.p.c. double detectors. *Figure 4* shows the plots of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ against conversion for the P21–P24 series. The observed $\bar{M}_n$ values increase with monomer conversion and these values come above the dashed line. These results suggest that the anionic polymerization of BMA at −78°C proceeds with not only slow initiation but slow propagation. No termination or transfer is involved in this mechanism.

We can conclude from the experiments described above that the polymerization temperature has a significant effect on the living nature of the BMA polymerization in THF. Consequently, we also carried out the anionic polymerization of BMA at −45°C (P31–P33, see *Table 3*). The monomer conversion reaches 42% after 1 h and 62% after 7 h. A typical g.p.c. profile of P31 is shown in *Figure 2*; its distribution pattern is unimodal. Products P31–P33 have relatively narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n = 1.20$). The number of phenyl groups in each of these products was close to 2.0 per molecule. *Figure 5* shows the plots of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ against conversion for the P31–P33 series. The observed $\bar{M}_n$ values increase in direct proportion to monomer conversion and agree well with the calculated values (represented by the dashed line). The $\bar{M}_w/\bar{M}_n$ values are almost constant regardless of the increase in monomer conversion. Therefore, the DPB–Mg initiator induces an ideal living anionic polymerization of BMA in THF at this polymerization temperature. In order to achieve almost 100% conversion within a short time, it may be better to adopt a polymerization temperature between 0 and −45°C.

The structure of the DPB–Mg complex was investigated by spectroscopic analysis. *Figure 6* shows the ^{1}H n.m.r. spectrum of the DPB–Mg complex in C_6D_6. In addition to the signals of the phenyl (6.6–7.4 ppm) and methylene (2.09 ppm) protons of DPB–Mg, the spectrum exhibits absorptions assignable to THF (signals a and b). From the integrated peak intensities, the DPB–Mg complex was determined to be present in the form DPB–Mg·2THF. Moreover, the Mg content of the DPB–Mg complex was 6.2% as determined by

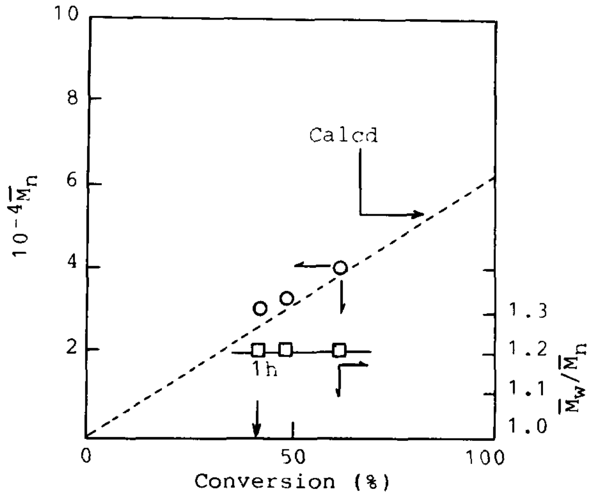


Figure 5 Plots of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ against conversion for the P31–P33 series

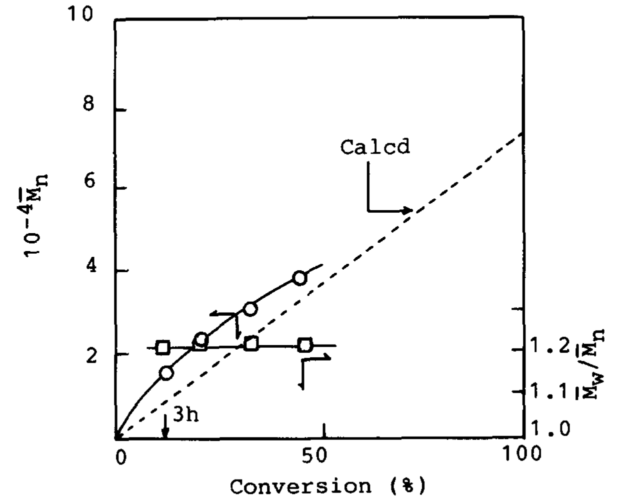


Figure 4 Plots of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ against conversion for the P21–P24 series

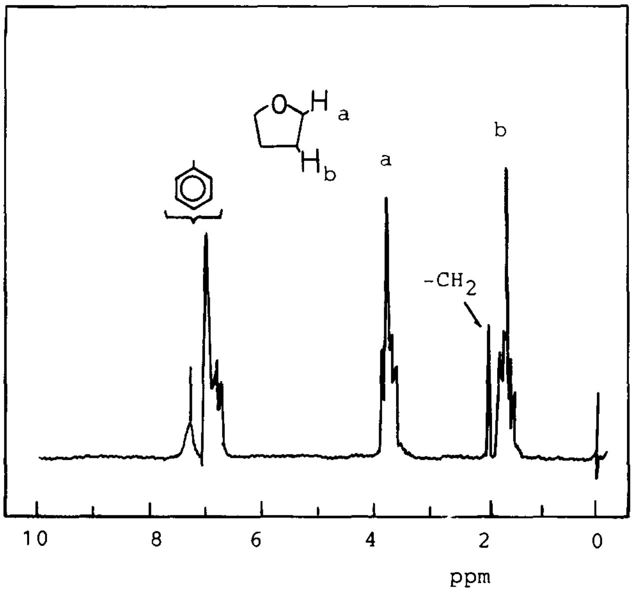


Figure 6 ^{1}H n.m.r. spectrum of the DPB–Mg complex in C_6D_6

Table 3 Anionic polymerization of BMA at −45°C[a]

Experiment number	Feed (mol l^{-1}) $10^4[\mathrm{I}]_0$	$10^2[\mathrm{M}]_0$	Time (h)	Conversion (%)	$10^{-4}\bar{M}_n$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$
P31	1.386	3.09	1	41.9	2.8	1.20
P32	1.386	3.09	3	49.1	3.2	1.20
P33	1.386	3.09	7	62.0	4.0	1.20

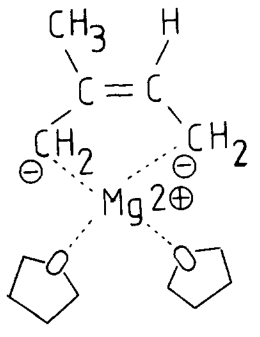
[a] Polymerized in THF (80 ml)

chelatometric titration using EDTA. On the assumption that this initiator has the empirical formula DPB–Mg·2THF, the calculated Mg content is 6.5%. The observed and calculated Mg contents are therefore in good agreement. The THF solution of DPB–Mg complex is red ($\lambda_{max} = 378$ nm). This suggests that the terminal carbanions give rise to resonance structures with the conjugated phenyl groups. It was mentioned earlier that formation of this complex is initiated by bifunctional carbanions.

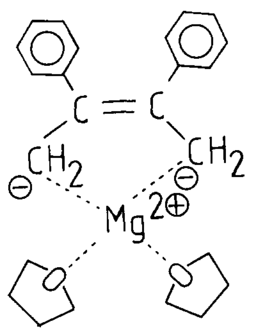
As is well known, Grignard reagents take part in a Schlenk-type equilibrium[21,22]

$$2RMgX \rightleftharpoons MgX_2 + R_2Mg$$

Stucky and Rundle[23] studied in detail the structural properties of the Grignard system C_6H_5MgBr in diethyl ether by X-ray diffraction. In the crystalline state $C_6H_5MgBr \cdot 2C_4H_{10}O$ consists of a magnesium atom tetrahedrally coordinated to two diethyl ether molecules, a phenyl group, and a bromide ion. They also determined the steric structure of $(C_6H_5)_2Mg \cdot 2C_4H_{10}O$ using the same method. According to their reports, single crystals of the phenylmagnesium bromide ditetrahydrofuran complex have been isolated by F. Schröder at the Institut für Anorganische Chemie der Technischen Hochschule, Braunschweig. In the 1960s Ramsden and Engelhart[24–26] found that some conjugated dienes reacted with metallic magnesium on heating in THF to give organomagnesium compounds named 'diene–magnesium compounds'. As part of the studies on diene–magnesium compounds, Takase *et al.*[27] investigated the reaction of isoprene with magnesium to prepare the 'isoprene–magnesium compound' and subsequently studied its reactivity towards aldehydes and ketones. In their reports, the chemical structure of the isoprene–magnesium compound in the crystalline state was speculated to have the form given by structure (**a**):



a



b

So, we can speculate that the DPB–Mg·2THF complex takes the form given by structure (**b**) in the crystalline state, given the above references and our results.

We speculated that the reactivity in anionic propagation of the DPB–Mg complex was attributable to two active species and attempted to show this by achieving scission of the central double bond of PBMA. The g.p.c. distribution for the ozonolysis product of PBMA showed the same pattern as that for the original PBMA. The DPB–Mg complex possesses phenyl groups at the 2,3-butadiene positions as shown in structure (**b**). So, the double bond at the central position of PBMA is stabilized by conjugation with these phenyl groups. Next, we carried out the oxidation of the double bond using peroxybenzoic acid and subsequently the degradation of the 1,2-glycol units produced by the oxidation. The ozonolysis product was also treated with peroxybenzoic acid. We observed no variations in the g.p.c. profiles of both final products compared to the original PBMA. The double bond, epoxide, and 1,2-glycol moieties could not be detected from *FT*i.r. owing to the fact that we had only extremely small quantities. The scission of double bonds using sodium naphthalenide was unsuccessful in our experimental conditions. It is necessary to investigate this idea by an improved method.

Macrocyclic polymers would be expected to be interesting because of their topologies. In macrocyclic polymers, in contrast to linear polymers, all structural units of the chain are chemically and physically equivalent. A synthetic approach to these may be through the coupling of dichlorosilyl compounds with PBMA living dianions initiated by the DPB–Mg complex. The results obtained will be reported in the near future.

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