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Synthesis of Poly(isobutylene-*b*-styrene) Block Copolymers by Thermolysis of Ozonized Alkene-Ended Polyisobutylenes in the Presence of Styrene

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ABSTRACT: Polyisobutylene (PIB) possessing alkene end groups was ozonized. NMR spectroscopy showed that trioxolanes and tetroxolanes were the main products and that these products were relatively stable. Thermolysis of the ozonolysis products generated radicals, which were shown by ESR spin-trapping experiments to be alkyl and oxyalkyl species. Thermolysis in butyl propionate solution also generated radicals with structures consistent with those expected of species arising from hydrogen abstraction from solvent. Thermolysis in the presence of methyl methacrylate (MMA) or styrene (S) led to polymerization of both. Size exclusion chromatography (SEC) and gradient polymer elution chromatography (GPEC) were used to investigate the possibility that the newly formed polymer might be attached to PIB. In the case of MMA polymerizations, the final product was a blend of the two homopolymers: no evidence for block copolymers could be seen by SEC or GPEC. In contrast, both SEC and GPEC indicated that a large fraction of the newly formed polystyrene was attached to PIB, most probably in the form of P(IB-*b*-S) block copolymer.

Introduction

Ozonolysis of alkenes in nonparticipating solvents generally yields various peroxidic species, typically the six-membered ring 1,2,4,5-tetroxolane (cyclic diperoxide), the five-membered ring 1,2,4-trioxolane, and various cyclic and linear polyperoxides.[1−7] Cafferata et al. showed that the 1,2,4,5-tetroxolanes can generate radicals upon thermolysis and successfully measured k_d for the thermolysis, to radicals, of acetone cyclic diperoxide.[8−13] We have recently studied these radicals and have shown that thermolysis of 1,2,4,5-tetroxolanes can be used to initiate polymerization of vinyl monomers.[14] Similarly, Pryor et al. thermolyzed 1,2,4-trioxolanes, which yielded radicals that they were able to study using ESR spectroscopy.[15−17] Ozonolysis of tetrasubstituted alkenes usually does not give 1,2,4-trioxolanes but gives high yields of 1,2,4,5-tetroxolanes and the oligomeric products.[1−4] Thus, ozonolysis of tetramethylethene yields product mixtures comprising acetone cyclic diperoxide, acetone cyclic triperoxide, and open-chain polyperoxides, which upon thermolysis at moderate temperatures yield carbon- and oxygen-centered radicals that are able to initiate radical chain growth polymerizations.[14,18,19]

Following these observations, we have considered that if the alkene double bond were to be situated at a polymer (or oligomer) chain end, or as an in-chain unit, then thermolysis of the ozonized polymer or oligomer should yield polymeric radicals. These radicals should be capable of initiating polymerization from a preformed polymer chain end. Such polymerizations would then yield a block copolymer. With this hypothesis in mind we have, in this report, focused on the preparation of polyisobutylene (PIB) block copolymers.

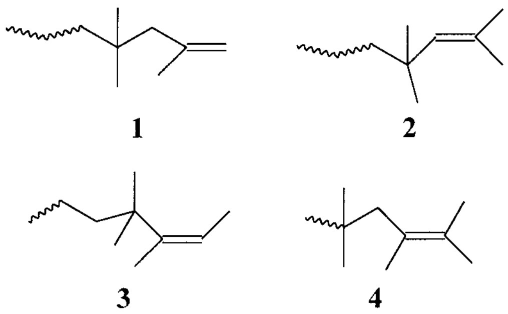

Figure 1. End group structures found in PIB prepared by nonliving cationic polymerization.

While block copolymers featuring PIB blocks are well-known, they are usually prepared by living polymerization techniques (for recent examples see refs 20−26). Copolymerization of monomers that are not amenable to cationic polymerization involves changing the chain end to a group suitable for the initiation of the second block.[27−30] PIB as prepared commercially by a nonliving route contains alkene end groups, which can be ozonized to give species that are capable of generating radicals, following thermolysis. Storey and Donnalley recently reported the use of ozonolysis to generate PIB with carbonyl chain-end functionality.[31] Thermolysis of these ozonized oligomers ought then to yield radicals, and these radicals may be situated at the chain ends. If the thermolysis is conducted in the presence of monomer, these PIB radicals should initiate polymerization from PIB chain ends to yield PIB block copolymers. In effect, this is an extension of the well-known method of changing the end group structure following a living cationic polymerization but the proposed methodology

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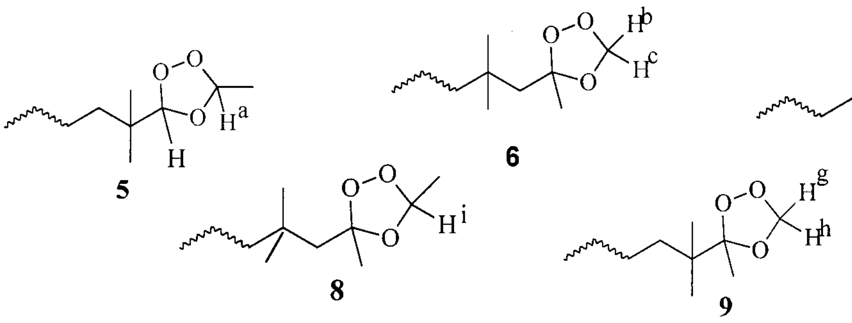

Figure 2. Trioxolanes and cross-trioxolanes derived from PIB end groups by ozonolysis. The products are derived from coupling of: **5**, macrocarbonyl oxide from **3** + acetaldehyde; **6**, macrocarbonyl oxide from either **1** or **4** + formaldehyde; **7**, macrocarbonyl oxide from **2** + formaldehyde; **8** macrocarbonyl oxide from either **1** or **4** + acetaldehyde; **9**, macrocarbonyl oxide from either **3** + formaldehyde

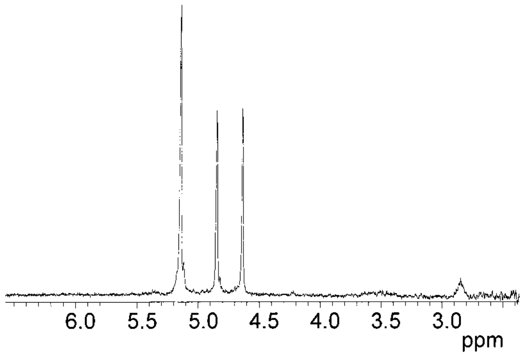

Figure 3. ^{1}H NMR spectrum of PIB prior to ozonolysis: expansion of the alkene region.

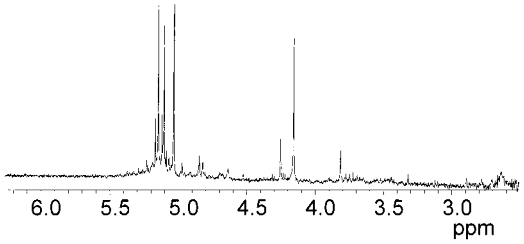

Figure 4. ^{1}H NMR spectrum of ozonized PIB: expansion of 1,2,4-trioxolane region.

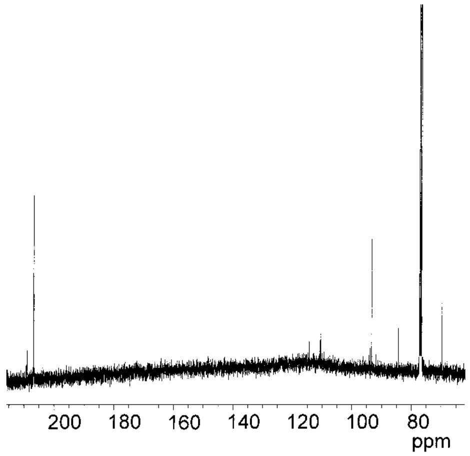

Figure 5. ^{13}C NMR spectrum of ozonized PIB.

does not require that PIB be prepared under living conditions. The following report details our work in this area with methyl methacrylate (MMA) and styrene (S).

Results

Ozonolysis of PIB. The end groups of PIB prepared by nonliving cationic polymerization typically contain structures **1**−**4** (Figure 1).[32] If one assumes that acetone, produced on cleavage of the primary ozonide derived from **2** and **4**, does not react with carbonyl oxides,[1] then these structures upon ozonolysis will lead to 1,2,4-trioxolane end groups **5**−**9** (Figure 2) and low molecular weight 1,2,4-trioxolanes. The low molecular weight 1,2,4-trioxolanes are, however, volatile and are removed by vacuum stripping.

The ^{1}H NMR spectrum of PIB prior to ozonolysis is shown in Figure 3. Peaks at 5.15, 4.62, and 4.84 ppm correspond to the proton signals from the end groups **2** and **1**, respectively[33] These peaks are absent in the ^{1}H NMR spectrum of the ozonized material, shown in Figure 4.

Chemical shifts for protons attached to the trioxolane ring in pure ozonides characteristically fall within the range 4.80−6.20 ppm.[4] Ozonolysis of a sample of high end group **3** content (Hyvis from BP Chemicals) gave a product in which the ^{1}H NMR spectrum (not shown) contained mainly a peak at 4.15 ppm, which can be tentatively assigned to H^a in ozonides of structure **5**. Similarly, the resonance at 4.25 ppm can be assigned to H^i in structure **8**. The five protons attached to 1,2,4-trioxolanes **6** and **7**, H^b−H^h (five resonances since H^b and H^c are magnetically equivalent to H^g and H^h), are observed at 5.04, 5.11, 5.13, 5.15, and 5.18 ppm. These chemical shifts are in good agreement with data reported for similar low molecular weight 1,2,4-trioxolane.[16] **6**, **9**, and **7** are expected from reaction of macro carbonyl oxides with methanal, while **5** and **8** are expected from reactions of the macro carbonyl oxides with ethanal (Figure 2).

The ^{13}C spectrum (Figure 5) shows peaks at 69.88, 84.42, and 93.38 ppm as expected for structures **5**−**9**.[16] However, minor peaks also appear at 110.44, 110.83, and 115.15 ppm. Downfield peaks of similar chemical shift, $\delta = 110.97$ ppm, are also observed in the ^{13}C NMR spectrum of a model 1,2,4,5-tetraoxolane, 3-methyl-2-propanone diperoxide (**10**), which we have separately synthesized. Therefore, it is likely that the ozonized PIB also contains 1,2,4,5-tetraoxolane end groups formed from the reaction of macro carbonyl oxides and acetone carbonyl oxide or by dimerization of two macro carbonyl oxides. This latter hypothesis is supported by the fact that, upon ozonolysis, the number-average molar mass, M_n, measured by SEC increases slightly from 1160 to 1300 g mol^{-1} as would be expected following a small degree of reaction between two macro carbonyl oxides or a macro carbonyl oxide and a macro aldehyde.

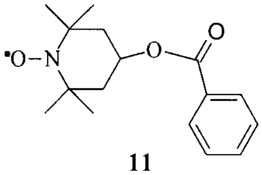

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Figure 6. TEMPO phenylate: a chromophore-containing spin trap.

Aldehyde end groups give rise to NMR signals at 9.51 (^{1}H) and 206.90 ppm (^{13}C) and methyl ketone end groups to NMR signals at 209.22 ppm (^{13}C). Thus, the ^{13}C spectrum of ozonized PIB further indicates that polymeric 1,2,4-trioxolane and 1,2,4,5-tetraoxolanes are formed at the oligomer chain end, following ozonolysis. There is also a strong carbonyl band in the IR spectrum of ozonized PIB at 1725 cm^{-1}, which is absent in the IR spectrum of PIB before ozonolysis.

Thermolysis of Ozonized PIB in the Presence of Spin Traps. The ozonized PIB was heated in the presence of **11**, a spin trap containing a chromophore (Figure 6).

Following thermolysis, the groups of ^{1}H NMR signals around 5.00 ppm, present prior to thermolysis, were absent and were replaced by signals at 3.50 (s), 4.48 (s), 7.45 (s), 7.56 (s), and 8.02 ppm (d), which are characteristic of **11**. Similarly, the ^{13}C resonances assigned to 1,2,4,-trioxolane and 1,2,4,5-tetraoxolane carbons were also absent after thermolysis in the presence of **11** and were replaced by peaks at 128.02, 129.54, 133.50, and 166.27 ppm. The signals arising from the aldehyde and ketone end groups remained, although the peak assigned to ketone end groups appeared to be larger, relative to the peak assigned to the aldehyde end groups. While these NMR analyses imply that macro radicals have been produced and that they are trapped by **11**, they do not provide unequivocal evidence. To gather more conclusive evidence, the thermolyzed sample was analyzed by SEC with dual RI and UV detection. A moderately strong UV signal, which superimposed with the chromatogram derived from the RI detector, was observed. This UV signal arises from the phenyl group of **11** located at the chain end.

Next the nature of the radicals produced during thermolysis was investigated. Thus, the ozonized PIB was thermolyzed in the presence of both *N*-*tert*-butyl-α-phenylnitrone (PBN **12**) at 100 °C and 2,4,6-tri-*tert*-butylnitrosobenzene (TTBNB **13**) at 90 °C, both in butyl propionate. PBN was selected because of its superior ability to trap oxygen-centered radicals although it also traps carbon-centered radicals. TTBNB preferentially traps carbon-centered radicals and provides more information on the structure of the original radical than PBN owing to the proximity of its atoms to the unpaired electron in the nitroxyl adduct and to the narrower line widths associated with its nitroxyl adducts.

The ESR spectrum obtained in the presence of PBN, which increases in intensity with time, is shown in Figure 7. The spectrum can be simulated with hyperfine parameters of a(N) 1.460 and $a(\mathrm{H}_\beta)$ 0.306 mT. These parameters are close to those expected for a PBN adduct of a carbon-centered radical. However, the lack of symmetry in the spectrum and the broadness of the hyperfine lines indicate that this spectrum almost certainly arises from a mixture of adducts, which could well include a small percentage of an adduct of an oxygen-centered radical as well as adducts of, perhaps, several carbon-centered radicals.

Figure 7. ESR spectrum obtained after thermolysis of ozonized PIB at 100 °C in the presence of the radical trap, PBN.

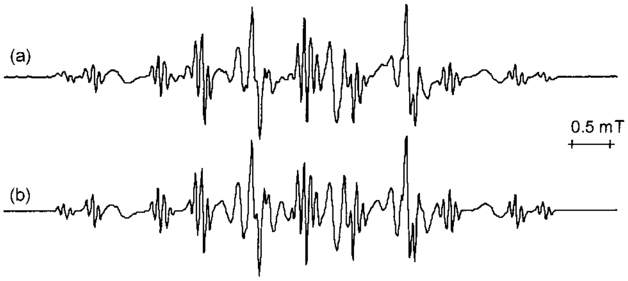

Figure 8. ESR spectrum of ozonized Ultravis PIB thermolyzed in the presence of TTBNB at 90 °C in butyl propionate: (a) experimental spectrum and (b) simulated spectrum.

Considerably more information was obtained when the experiment was repeated in the presence of TTBNB. The spectrum obtained after 5 min thermolysis is shown in Figure 8, together with its simulation.

The spectrum consists of a complex mixture of seven adducts with considerable overlapping of the hyperfine lines of each adduct. However, the simulation (Figure 8b) reveals the presence of the TTBNB adduct of the methyl radical (5%, characterized by coupling to three equivalent β-protons, a(N) 1.306, $a(3\mathrm{H}_\beta)$ 1.225, and $a(2\mathrm{H}_\mathrm{m})$ 0.078 mT).

Also present are the nitroxyl (5%, a(N) 1.324, $a(2\mathrm{H}_\beta)$ 1.830, and $a(2\mathrm{H}_\mathrm{m})$ 0.073 mT) and anilino (29%, a(N) 1.011, $a(2\mathrm{H}_\beta)$ 0.200, and $a(2\mathrm{H}_\mathrm{m})$ 0.189 mT) adducts of a $^\bullet\mathrm{CH_2R}$ radical (characterized by coupling to two equivalent β-protons) and an anilino adduct (10%, a(N) 1.010 and $a(2\mathrm{H}_\mathrm{m})$ 0.192 mT) of a $^\bullet\mathrm{CR_3}$ radical (characterized by the absence of coupling to any β-protons). All of these carbon-centered radicals (i.e., $^\bullet\mathrm{CH_3}$ and the macro $^\bullet\mathrm{CH_2R}$ and $^\bullet\mathrm{CR_3}$ radicals) are expected to arise via cleavage of the O−O bond during thermolysis followed by β-scission of the resulting alkoxyl radicals.

In addition, there are the nitroxyl (26%, a(N) 1.378, $a(\mathrm{H}_\beta)$ 2.161, and $a(2\mathrm{H}_\mathrm{m})$ 0.076 mT) and anilino (7%, a(N) 1.083, $a(\mathrm{H}_\beta)$ 0.152, and $a(2\mathrm{H}_\mathrm{m})$ 0.166 mT) adducts of a $^\bullet\mathrm{CHR_2}$ radical (characterized by coupling to a single β-proton). A $^\bullet\mathrm{CHR_2}$ radical is not expected via β-scission reactions and almost certainly results from the abstraction of a methylene proton from the solvent (butyl propionate). The final component is a nitroxyl adduct (18%, a(N) 1.346, $a(2\mathrm{H}_\beta)$ 1.432, and $a(2\mathrm{H}_\mathrm{m})$ 0.076 mT) of a $^\bullet\mathrm{CH_2R}$ radical (characterized by coupling to two equivalent β-protons) with slightly unusual hyperfine parameters for an adduct of a simple primary alkyl radical; it could well be the adduct of the $^\bullet\mathrm{CH_2CH_2C(O)O(CH_2)_3CH_3}$ radical formed by hydrogen abstraction from the ester solvent.

Polymerizations Initiated by Ozonized PIB. From these investigations it is clear that ozonized PIB, when thermolyzed, produces macroradicals, which arise from cleavage and secondary reactions of 1,2,4-trioxolane and 1,2,4,5-tetraoxolane end groups. It was therefore envisaged that these radicals could initiate polymerization of vinyl monomers and that the products should contain at least a fraction of the polymer in the form of a block

Table 1. Yields, Average Molecular Weights (M_n), and Polydispersities of Products of PIB Ozonate-Initiated Polymerizations

PIB treatment	polym temp (°C)	monomer	M_n (g mol^{-1})	M_w/M_n	S or MMA content (mol %)[a]
nonozonized			1160	1.7	0
ozonized			1300	1.9	0
ozonized	60	S	2230	3.8	28
ozonized	80	S	2570	4.8	45
ozonized	100	S	4400	4.2	76
ozonized	120	S	2830	4.6	67
ozonized	140	S	3255	3.8	67
ozonized	100	MMA	3170	3.8	47
ozonized	140	MMA	2780	2.9	56

[a] Styrene or MMA content of the product calculated by ^{1}H NMR spectroscopy.

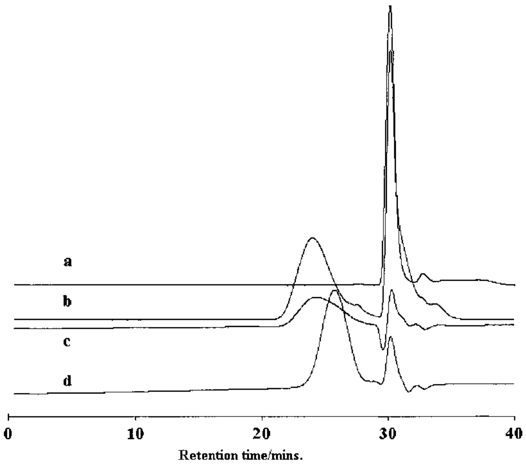

Figure 9. SEC chromatograms of the reaction products following thermolysis (at 140 °C) of ozonized PIB in the presence of S: (a) UV detector response from the PIB starting material; (b) UV detector response from the reaction mixture; (c) RI detector response from the reaction mixture; (d) RI detector response from the starting material.

copolymer. The molecular weights of polymers resulting from such experiments are shown in Table 1. As can be seen clearly from the data in Table 1, the ozonized reaction mixtures do indeed initiate polymerization of both MMA and S, and the M_n's as measured by SEC increase after thermolysis in the presence of these monomers.

Chromatographic Analysis: Styrene Polymerizations. Figure 9 shows an example of an SEC chromatogram obtained on initiating styrene polymerization with ozonized PIB at 140 °C. Also shown is the chromatogram of the starting PIB material. Clearly, new material of higher molecular weight is present following the reaction. Polymerization at this temperature gave essentially superimposable UV and RI traces as would be expected for a material composed of one compositional component. However, SEC is unable to provide compositional information in this instance.

Some of the most powerful techniques for copolymer analysis are the various types of liquid chromatography.[33] Some of these techniques, e.g., gradient polymer elution chromatography (GPEC), are well able to distinguish between block (or graft) copolymers and mixtures of homopolymers.[35] Therefore, to prove conclusively the formation of IB−S block copolymer in the above-mentioned experiments, we employed reverse-phase GPEC analysis. The separation of PIB and PS homopolymers was achieved by first injecting the sample, dissolved in tetrahydrofuran (THF), into an aqueous/DMA eluent at which point the sample precipitated. The eluent was then gradiated to 100% DMA. The PS component could then be eluted isocratically. Following this isocratic period, the eluent was then gradiated to 100% THF in order to elute the PIB fraction. Chromatograms derived from PS and PIB homopolymers and from the reaction products obtained at polymerization temperatures ranging from 60 to 140 °C, which are presumed to contain also some IB−S block copolymer, are shown in Figures 10−14.

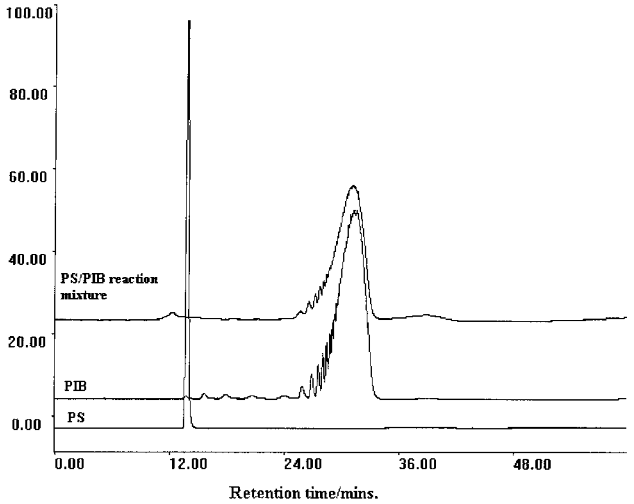

Figure 10. GPEC chromatograms of starting PIB, a PS standard, and product from polymerization of S initiated by ozonized PIB at 60 °C.

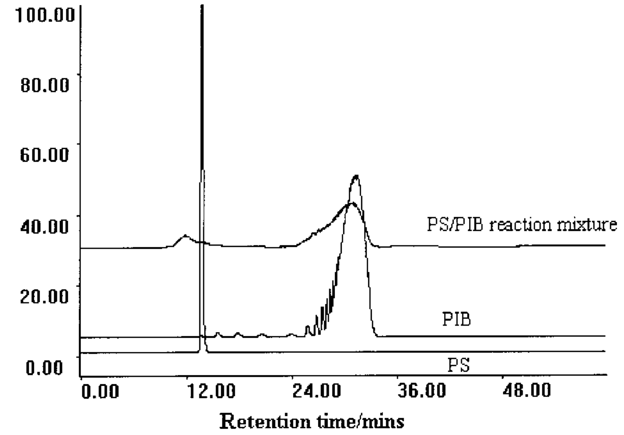

Figure 11. GPEC chromatograms of starting PIB, a PS standard, and product from polymerization of S initiated by ozonized PIB at 80 °C.

As can be seen from these figures, the reverse-phase analysis gave excellent chromatographic separation of the homopolymer components; each chromatogram clearly shows the presence of homopolymers. However, with the exception of that obtained from the products of polymerization at 60 °C (Figure 10), the chromatograms show strong evidence for the presence of a third component, which has a distribution of retention times that are intermediate between those of the two homopolymers. In the chromatograms of the products produced at 80, 120, and 140 °C, this material is seen as a pronounced shoulder on the PIB peak, or as extensive broadening of this peak, toward lower elution times.

However, in the chromatogram of the reaction mixture prepared at 100 °C an almost fully resolved peak,

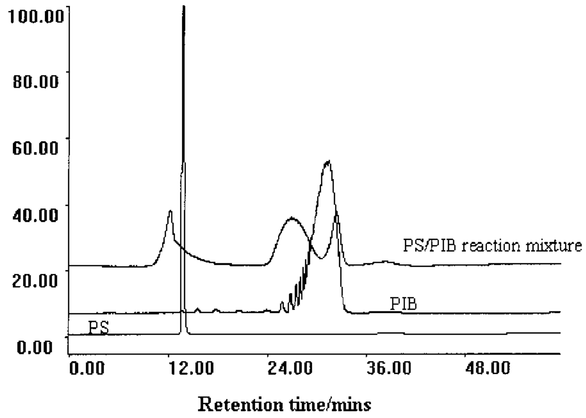

Figure 12. GPEC chromatograms of starting PIB, a PS standard, and product from polymerization of S initiated by ozonized PIB at 100 °C.

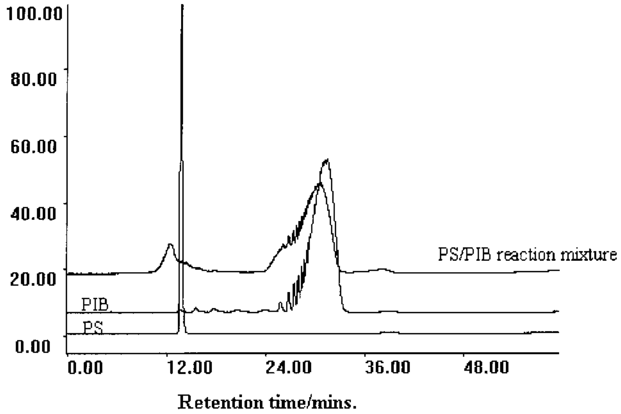

Figure 13. GPEC chromatograms of PIB, a PS standard, and product from polymerization of S initiated by ozonized PIB at 120 °C.

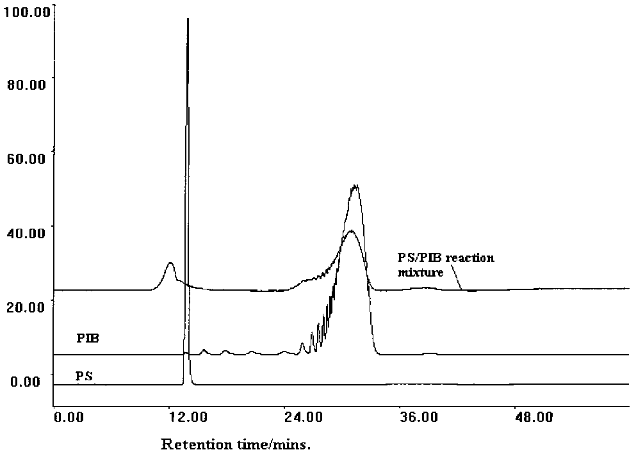

Figure 14. GPEC chromatograms of starting PIB, a PS standard, and product from polymerization of S initiated by ozonized PIB at 140 °C.

arising from block copolymer, can be seen. The optimum temperature, therefore, for the production of IB−S block copolymer by the thermolysis of ozonized PIB in the presence of S is 100 °C. If one assumes that all of the block copolymer elutes just before the PIB, i.e., gives rise to the additional peak alongside the peak from PIB at slightly lower retention time, then block copolymer accounts for at least 40% of the total mass of this sample. However, each of the chromatograms shows further evidence for block copolymer formation in the vicinity of the PS peak. That is to say, examination of the peaks arising from the PS-rich fractions in the polymerization products reveals them to be highly asymmetric and suggests that they possess shoulders that could also be a consequence of block copolymer formation.

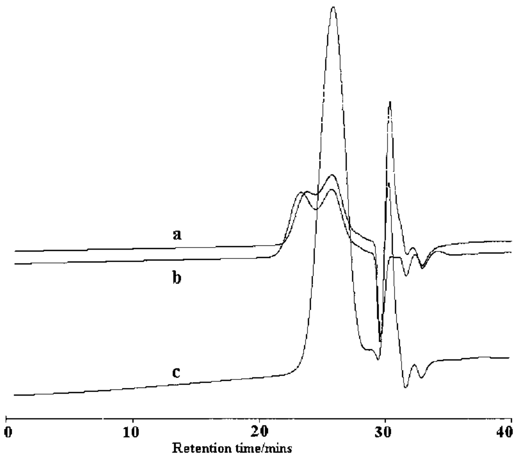

Figure 15. SEC chromatograms (RI responses) of the reaction products following thermolysis, in the presence of MMA, of the ozonized PIB: (a) thermolysis at 140 °C, (b) thermolysis at 100 °C, and (c) the PIB starting material.

We thus conclude that block copolymer rich in IB gives rise to GPEC peaks just to the low elution volume side of the PIB peak, while block copolymer rich in S gives rise to peaks just to the high elution volume side of the PS peak. Overall, we conclude that these GPEC analyses provide unequivocal evidence that ozonized alkene ended-PIB can be used as a precursor to a radical macroinitiator that, in turn, can be used to prepare poly(IB-*b*-S) materials.

Chromatographic Analysis: MMA Polymerizations. In contrast to the results with styrene, polymerizations of MMA initiated by ozonized PIB do not produce significant amounts of block copolymer. Instead, a blend of the two homopolymers is produced. Figure 15 shows the SEC chromatograms of the products of polymerizations carried out at 100 and 140 °C. There are clearly two distributions present giving bimodal peaks in each case. The presence of homo-PIB can also be inferred from the fact that one of these peaks superimposes with the peak derived from the unmodified PIB.

Reverse-phase GPEC was used to separate the homopolymers and thus also to further establish the nature of these products. Figure 16 shows the chromatograms derived from polymerizations conducted at 100 and 140 °C along with chromatograms of the PIB starting material and a PMMA standard. The chromatograms of the materials derived from the polymerizations clearly show the presence of PMMA homopolymer, which elutes between 10.0 and 13.5 min, and the PIB starting material, which elutes between 13.5 and 30 min, but show no evidence for any block copolymer.

Discussion

We have shown that thermolysis of ozonized PIB yields radicals that can initiate polymerization of vinyl monomers. This is in good agreement with the previous work of Pryor et al., who showed that 1,2,4-trioxolanes of low molecular weight alkenes, on thermolysis at relatively low temperatures, generate radicals.[5,6,15−17]

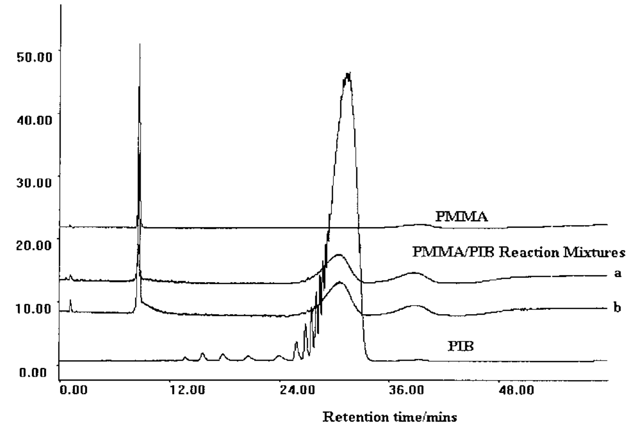

Figure 16. GPEC chromatograms of the starting PIB, a PMMA standard, and products of polymerization of MMA initiated by ozonized PIB at (a) 140 and (b) 100 °C.

The NMR spectra of the ozonized PIB show that 1,2,4-trioxolanes are the predominant product of these ozonolyses, although some evidence for the production of 1,2,4,5-tetroxolanes can also be inferred from the ^{13}C spectra. The radicals generated are alkyl radicals, which can initiate polymerization or transfer to solvent. ESR spectra of species spin-trapped with **13** has also shown the existence of radicals derived from esters. Since ester radicals and methyl radicals cannot be attached to a PIB chain, initiation of vinyl polymerization by these radicals will lead predominantly to homopolymer. (There is a possibility also, of course, of a homopolymer radical terminating by combination with a propagating block radical to give block copolymer.)

The differing behaviors of the two monomers, S and MMA, could have several explanations. First, S is more compatible with PIB (in that the polarity of S and PIB are similar) than MMA is with PIB, so that it is possible that the local monomer concentration around the macro radical derived from the PIB is higher when S is used than when MMA is used. Second, since ESR spectroscopy has shown that transfer to the ester solvent occurs in the absence of monomer,[14] transfer may be more significant in the MMA polymerizations. These polymerizations are carried out at relatively high temperatures at which transfer reactions are known to be favored. Also, transfer to monomer is more probable in radical polymerizations of MMA than in radical polymerizations of S, since MMA contains allylic hydrogens whereas S does not. The significance of transfer reactions in the polymerizations with MMA is also supported by the relatively low average molecular weights of the final products. The third explanation is that the usual termination reactions (combination for S and disproportionation for MMA) favor production of block copolymer chains for styrene, through coupling of either P(IB-*co*-S) radicals or PIB macroradicals with homo-PS or P(IB-*co*-S) radicals. Therefore, even if transfer or initiation by non-PIB radicals is significant, in polymerizations of S termination by combination provides a second route to the production of block copolymer. Termination by disproportionation in the MMA polymerizations will tend to favor homopolymer formation.

Currently, it is not possible to establish which of the above features are dominant. However, it is likely that all three play a role. It is also significant that each of these features tends to favor block copolymer formation when ozonized PIB is used to initiate polymerization of S, and production of a blend of homopolymers when ozonized PIB is used to initiate polymerization of MMA.

Table 2. Solvent Program Used for GPEC Analysis

time (min)	dimethylacetamide (%)	water (%)	THF (%)
0	95	5	0
1	100	0	0
15	100	0	0
30	0	0	100
50	0	0	100
60	95	5	0

Experimental Section

Materials. Ultravis PIB was a gift from BP Amoco (Grangemouth, UK). MMA and S (Aldrich) were washed with two equal volumes of 2% NaOH(aq) and two equal volumes of deionized water. Both monomers were then distilled under reduced pressure. Butyl propionate was distilled prior to use. The benzyl ester of hydroxy-TEMPO was a gift from Akzo-Nobel (Deventer). Solvents for GPEC were HPLC grade (Fisher Chemicals) and THF for SEC was GPC grade (Fisher). All other chemicals were used as supplied by Aldrich.

Spectroscopic and Chromatographic Analyses. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL GSX 400 MHz spectrometer using $CDCl_3$ as the solvent. IR spectra were recorded on a Nicolet 205 FT-IR instrument using a solution cell or a Nujol mull. ESR spectra were recorded on a Bruker EMX *X*-band spectrometer operating with 100 kHz magnetic field modulation, a modulation amplitude of 0.02 mT, and with spectrum accumulation over 2−9 scans. Thermolysis was undertaken in situ employing the Bruker B-VT1000 variable temperature control system (accurate to ±1 K). Spectrum simulations were undertaken employing PEST WinSim[36] (a NIEHS public EPR software tool). The hyperfine splitting constants obtained from these spectral simulations are considered accurate to ±0.005 mT.

SEC was used to obtain estimates of the molecular weight distributions of the products. SEC measurements were carried out with RI and UV (260 nm) detectors at ambient temperature using THF as the solvent and toluene as a flow marker. Polymer Laboratories PlGel, 5 μm, 100 Å, and 2 × 60 cm low molecular weight columns were used with a flow rate of 1 $cm^3\ min^{-1}$. Sample concentrations were 2 mg cm^{-3}. The chromatograms were calibrated against polystyrene standards (Polymer Laboratories), styrene polymerizations, or PMMA standards, MMA polymerizations (Polymer Laboratories). Reverse-phase GPEC was used to separate the reaction mixture resulting from heating either MMA or S with the PIB ozonate. The conditions were as follows: column, 10 cm, Jones chromatography, C18, 4 μm; flow rate, 1 $cm^3\ min^{-1}$; temperature, 50 °C. The solvent program is given in Table 2.

Synthesis of 3-Methyl-2-propanone Cyclic Diperoxide (10). Concentrated sulfuric acid (10.60 cm^3) was added to 70% v/v hydrogen peroxide (2.40 g, 70.5 mmol) in acetonitrile (15 cm^3) at −20 °C in an acetone−dry ice bath with vigorous stirring. 3-Methyl-2-butanone (4.40 g, 52 mmol) in acetonitrile (10 cm^3) was added dropwise over 20 min to the vigorously stirred mixture. After a short while, a white solid began to precipitate out of solution. Stirring was continued at −20 °C for 1 h. The product was collected by filtration and washed thoroughly with water before being dried. MPDP (0.82 g, yield 8%) was obtained. The product was then recrystallized from warm methanol before being filtered once again and dried in a vacuum oven overnight.

Melting point: 120−122 °C.

^{1}H NMR: δ 0.98 ppm (d), δ 1.14 ppm (m), δ 1.70 ppm (s).

^{13}C NMR: δ 15.32 ppm, δ 16.07 ppm, δ 16.45 ppm, δ 27.35 ppm, δ 34.42 ppm, and δ 110.67 ppm.

MS: (EI) $m+/z$ = 129, 87, 86, 73, 71, 42.

IR (Nujol): 2900 cm^{-1} (s), 2890 cm^{-1} (s), 2853 cm^{-1} (s), 1278 cm^{-1} (m), 1131 cm^{-1} (m) 1032 cm^{-1} (m).

Spin Trapping of Ozonized and Thermolyzed PIB with the Benzyl Ester of Hydroxy-TEMPO. The benzyl ester of hydroxy-TEMPO (200 mg, 0.73 mmol) was dissolved in octane (25 cm^3) containing a few drops of ethyl acetate and added to ozonized PIB (11.50 g) The solution was then heated under a blanket of nitrogen for 6 h. After 6 h, the orange color of the solution had faded. The solvent was then removed under reduced pressure. To remove unreacted spin trap from the PIB, the polymer was dissolved in hexane (20 cm^3), methanol (20 cm^3) was then added, and the two layers were separated. The excess spin trap (orange) dissolved in the methanol layer and was thus removed. This was repeated three times. Hexane was then removed from the PIB under reduced pressure.

Spin Trapping of Ozonized and Thermolyzed PIB with Phenyl-*N*-*tert*-butyl-α-nitrone, 12, or Tri-*tert*-butylnitrosobenzene, 13. Ozonized PIB (1.00 g) and **12** (9.00 mg, 0.1 mmol) or **13** were dissolved in butyl propionate (1.00 cm^3). A sample was placed in an ESR tube and degassed with nitrogen for 5 min and then heated. ESR spectra were recorded as required over a period of 30 min.

Ozonolysis of PIB and Polymerization with Either S or MMA. In a typical procedure, PIB (23.00 g) was dissolved in pentane (50 cm^3) and cooled to −60 °C in a dry ice−acetone bath. Ozone was then bubbled through the solution at a rate of 0.3 g h^{-1} for 80 min. Nitrogen was then flushed through the system for 20 min to remove any excess ozone. The solvent was removed under reduced pressure, leaving ozonized PIB, a viscous liquid with a slight green color. A portion of this material (11.5 g) was then dissolved in butyl propionate (15 cm^{-3}), and either MMA (10.00 g, 0.1 mol) or S (10.0 g, 0.1 mol) was added. These solutions were then heated for 6 h under a blanket of nitrogen at the desired temperature. The contents of each flask were then dissolved in dichloromethane (20 cm^3) and precipitated into methanol. The products obtained were filtered, dried in a vacuum oven overnight, and weighed.

References and Notes

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