Polymer Bulletin 37, 785–790 (1996)

Polymer Bulletin

Determination of end groups in poly(methylmethacrylate peroxide) by fast atom bombardment mass spectrometry and IR spectroscopy

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Received: 3 June 1996/Revised version: 2 August 1996/Accepted: 14 August 1996

Summary

A detailed comprehensive investigation has been made to unequivocally analyse the end groups of a vinyl polyperoxide polymer namely, poly(methylmethacrylate peroxide), PMMAP, using Fast Atom Bombardment Mass Spectrometric (FABMS) technique.Further evidence to FABMS analysis has been sought from IR spectroscopic analysis on the same polymer. It has been found that PMMAP contains both hydroxyl and hydroperoxide end groups which has been explained by the chain transfer reaction of growing chain with the degradation product of PMMAP.

Introduction

Although polymer properties are determined largely by the backbone structure, the end groups also significantly influence the bulk properties of the polymers. For example, thermal stabilities are profoundly affected by the nature of the end groups (1-3). Precise knowledge about the end groups also helps in understanding the mechanism of polymerization particularly the termination and chain transfer reactions. Generally in most polymers, depending upon the nature of the initiating species, the end groups are established apriori. However, in relatively unstable polymeric systems the identification of the end groups is rendered difficult due to the degradation of the chains during polymerization itself. In such situations the end groups are likely to change and are mostly governed by the reaction conditions. Vinyl polyperoxides are striking examples of this type where the polymers degrade in a complex fashion during polymerization (4), as a result precise establishment of the end groups has remained elusive for a long time.

The only detailed study on the end group analysis of polyperoxide viz., poly(styrene peroxide),PSP, has been made by Cais and Bovey using ^{13}C NMR spectroscopy (5). Although it does give a fair amount of insight on the end groups, a few assignments could not be fully established. In view of the current resurgence of polyperoxides as fuels (6) and initiators (7), it has become imperative to establish the nature of the end groups unquivocally for a better understanding of their physico- chemical behaviour.

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The end groups can be determined accurately using Fast Atom Bombardment Mass Spectrometric (FABMS) analysis from the molecular ion peaks of the polymer (8,9). It is to be noted here that the polymer does not degrade during the FABMS analysis (10).However, the polymer molecular weight should lie within the detection range of the instrument (8). In order to have a detailed understanding of the end groups in polyperoxides, in the present study, FABMS analysis has been carried out on a polyperoxide namely, poly(methylmethacrylate peroxide), PMMAP. To support the results obtained from FABMS studies, IR spectroscopic analysis has also been performed.

Experimental Section

Synthesis of PMMAP

Freshly distilled MMA (50 mL) and recrystallised AIBN (0.01M) were placed in a PARR 1671 reactor and pressurized with 250 psi of oxygen. The polymerization was maintained at 50°C and the reaction was carried out with a constant stirring for 20 hrs. The PMMAP was precipitated from the reaction mixture using petroleum ether and was subsequently washed twice with 25 mL of the same non solvent followed by drying in vacuum. An average molecular weight of PMMAP ($\overline{M}_n$) is 1800.

FABMS analysis

The FAB mass spectrum were recorded on a JEOL SX 102/DA-6000 mass spectrometer using Argon/Xenon (6 kV) as the FAB gas. The accelerating voltage was 10 kV and the spectrum was recorded at room temperature. The m-nitrobenzyl alcohol was used as the matrix. The molecular weight scan limit was up to m/z 2500.

IR spectroscopy

The IR spectrum was recorded in CCl_4 on a Perkin-Elmer Spectrophotometer-597 instrument.

Results and Discussion

The peaks appearing in the FABMS spectrum at m/z 136, 137, 154, 289 and 307 were due to the matrix and hence not considered for the discussion.

In Figure 1, the positive FABMS of PMMAP is displayed and the corresponding structures for the peak assignments are presented in Table 1. The series of peaks at m/z 283 + n132 (n = 1-7) corresponds to the oligomers with hydroxyl and hydroperoxide end groups. It should be noted here that the quasi molecular ions of the oligomers appear as $(M+1)^{+\cdot}$ peaks. The formation of these end groups is explained in Scheme 1.

Initially, AIBN initiates the polymerization of PMMAP and hence forms the end groups (eq 1 & 2). The termination of such a growing chain with another AIBN radical (eq 2) is much more probable than the disproportionation mechanism proposed by Russell (5) for PSP. For disproportionation mechanism to occur, the peroxy radical has to be of secondary in nature which is not the present case (11). It is to be noted here that majority of polyperoxides including PMMAP degrade during the polymerization itself forming the products. PMMAP on degradation forms methyl pyruvate and formaldehyde as the products (12) (eq 3). This explains as to why in the FABMS analysis we did not detect the AIBN fragments as the end groups. During the propagation step, since there is always an excess of oxygen besides the peroxide radical being more stable than the alkyl radical, almost all the growing chains at any point of time will have a peroxide radical (eq 4). The termination reaction then occurs by the transfer of hydrogen from formaldehyde to the peroxide radical forming the hydroperoxide end groups (eq 4). The resultant formyl radical thus produced readily reacts with oxygen forming the peroxyformate radical which further initiates the polymerization (eq 5). It is to be noted here that the possibility of formaldehyde acting has a chain transfer agent has already been considered for PSP by

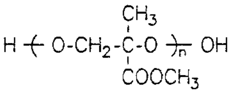
Polymer	Structure	quasi molecular ions [M+1] (m/z) at n =					
		2	3	4	5	6	7
PMMAP	 $H\text{-}(O\text{-}CH_2\text{-}\overset{CH_3}{\underset{COOCH_3}{C}}\text{-}O)_n\text{-}OH$	283	415	547	679	811	943

Table 1. Low Molecular weight oligomers detected in the positive FABMS of PMMAP

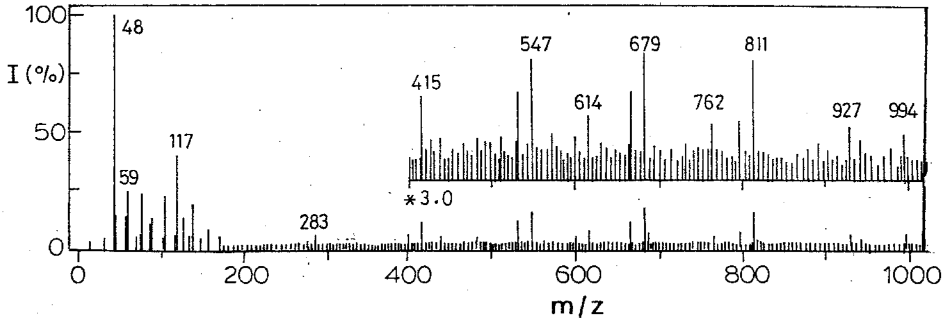
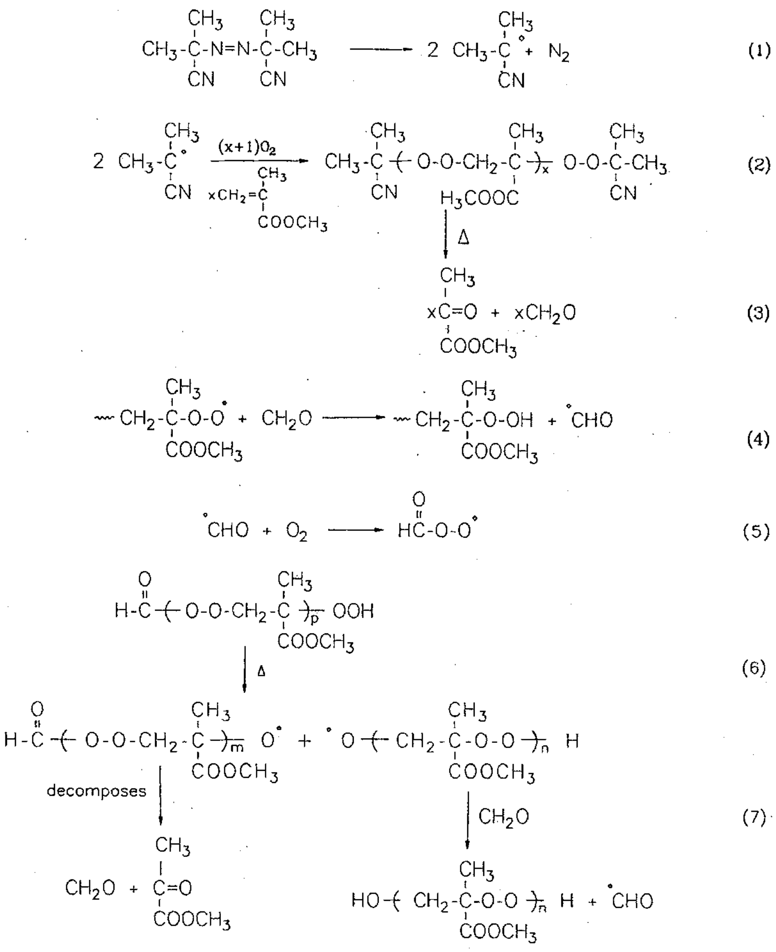


Fig.1. Positive FABMS of PMMAP.

Cais and Bovey(5). Although the formation of hydroperoxide end group is well established by FABMS analysis, we observe only hydroxyl groups in

Scheme 1. Mechanism of Polymerization of PMMAP.



the other end of the chain and not the formyl group. This discrepancy is explained as follows.

During polymerization the PMMAP formed with -CHO and hydroperoxide end groups undergoes further decomposition forming the alkoxy radicals (eq 6). Formaldehye once

again stabilizes the alkoxy radicals by hydrogen transfer forming the hydroxyl end groups (eq 7). The counter alkoxy radical having the -CHO end group, we believe undergoes unzipping forming the methyl pyruvate and formaldehyde (eq 7). To further substantiate the presence of hydroxyl and hydroperoxide end groups observed in FABMS, it was found from the IR spectrum of PMMAP (Figure 2) that a broad absorption exist between 3500-3000 cm^{-1} corresponding to the above mentioned end groups. Furthermore, absence of AIBN end groups is also substantiated from the IR analysis due to the undetection of the nitrile peak(5) at 2215 cm^{-1}.

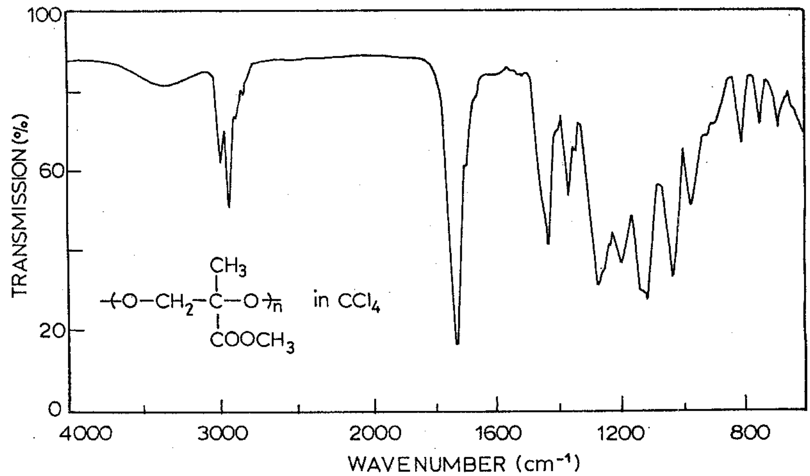


Fig.2. IR Spectrum of PMMAP in CCl_4

In figure 1, the other peaks detectred at m/z = 614,762,927 and 944 do not correspond to PMMAP oligomers, since the difference to the next higher molecular weight peak, does not correspond to the repeat unit molecular weight of PMMAP. Being a highly unstable polymer due to the presence of weak peroxy bonds in the backbone, we believe these peaks are due to the fragmentation of PMMAP molecular ions under FABMS condition.

Conclusions

Based on both FABMS and IR analysis of PMMAP, the presence of both hydroperoxide and hydroxyl end groups has been unequivocally established. It is to be mentioned here that polyperoxides are unique class polymers in that they undergo decompositon during polymerization itself, and the degradation products further act as chain transfer agents for the growing chain. Hence, the polymer obtained will not have the initiator derived end groups as commonly observed in vinyl polymers.

Acknowledgement

The authors are extremely thankful to the Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow, for recording the FABMS spectrum. .

References

1. Yoo Y, Kilic S, McGrath JE (1987) Polym Prepr (Am Chem Soc, Div Polym Chem) 28(1):272
2. Yoo Y, Kilic S, McGrath JE (1987) Polym Prepr (Am Chem Soc, Div Polym Chem) 28(2):358
3. Billmeyer FW Jr (1984) Textbook of Polymer Science. Wiley-Interscience, New York
4. Kishore K, Paramasivam S, Sandhya TE Unpublished work
5. Cais RE, Bovey FA (1977) Macromolecules 10:169
6. Kishore K, Mukundan T (1986) Nature 324:130
7. Shanmugananda Murthy K, Kishore K, Krishna Mohan V (1994) Macromolecules 27:7109
8. Montaudo G, Scamporrino E, Vitalini D (1991) Macromolecules 24:376
9. Montaudo G, Scamporrino E, Vitalini D (1989) Makromol Chem, Rapid Commun 10:411
10. Ballistreri A, Garozzo D, Giuffrida M, Montaudo G (1987) Anal Chem 59:2024
11. Lindsay D, Howard JA, Horswill EC, Iton L, Ingold KU, Cobbley T, Li A (1973) Can J Chem 51:870
12. Mukundan T, Kishore K (1987) Macromolecules 20:2382