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New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-transfer Agents (Inifers)

14. Characterization of Linear and Three-arm Star Polyisobutylenes by Degradative Oxidation

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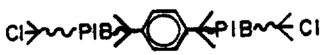
Summary

The molecular architecture of linear and three-arm star polyisobutylenes prepared by the use of bi- and trifunctional inifers (binifers and trinifers), respectively, has been analyzed. In particular, the number of polyisobutylene arms emanating from the central aromatic inifer residue and their molecular weights $\overline{M}_n$ have been determined. The analytical technique developed for this purpose consists of a selective and quantitative oxidative degradation of the central aromatic inifer residue with CF_3COOH-H_2O_2 mixtures in conjunction with $\overline{M}_n$ determinations before and after degradation.

Introduction

The polymerizations of isobutylene initiated with difunctional and trifunctional inifers (KENNEDY and SMITH 1980; KENNEDY et al. 1981) in conjunction with BCl_3 yield linear and three-arm star telechelic polymers carrying two or three $-CH_2(CH_3)_2Cl$ termini, respectively:



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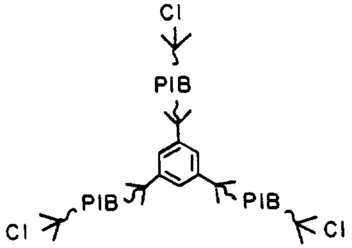

II

Considerable efforts have been made to characterize these molecules (KENNEDY and SMITH 1980; FEHERVARI et al. 1980; IVAN et al. 1980), in particular, to determine the number and molecular weights $\overline{M}_n$ of polyisobutylene (PIB) arms emanating from the central aromatic ring. The mechanism of inifer reactions leading to structures with internal aromatic rings has been

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discussed in detail (KENNEDY and SMITH 1980; KENNEDY et al. 1981). Inspection of these structures suggests that a key characterization method would consist of the following three steps: 1) Determination of the $\bar{M}_n$ of the starting polymer 2) Selective and quantitative destruction of the central aromatic ring, followed by 3) Determination of the $\bar{M}_n$ of the surviving fragments. The ratio of $\bar{M}_n$'s obtained before and after selective destruction of the central ring would give the number of PIB arms and, provided this number would be, respectively, 2.0 and 3.0 for the linear and three-arm star telechelics, would also conclusively support previous characterization data. This communication concerns a description of research in this direction, in particular, the development of an analytical method for the selective oxidative degradation of aromatic rings carrying PIB substituents with $CF_3COOH-H_2O_2$.

Experimental

To solutions of approximately one percent polyisobutylene in 50 ml CCl_4,were added under stirring in a hood, 24 ml of a solution of aqueous 30% H_2O_2 in trifluoroacetic acid and heated to reflux. Aliquots of the water layer were removed every 24 hours and titrated with a KI solution in order to ascertain the presence of peroxide. An additional 2.0 ml charge of H_2O_2 solution was added whenever the KI test for peroxide was negative. In this manner an excess of the trifluoroperacetic acid is insured.

The trifluoroacetic acid-H_2O_2 solution was prepared by adding 4 ml of 30% aqueous H_2O_2 to 20 ml of trifluoroacetic acid. Periodically samples of the CCl_4 layer were removed and allowed to evaporate to dryness. The residue was dissolved in THF and injected into a Waters high pressure G.P.C. instrument (Model 1-6000A pump, 5 μStyragel columns: 500Å, 1 x 10^3-1 x 10^6Å) for molecular weight determination. The calibration curve was constructed with PIB standards.

The coupling was carried out by dissolving the oxidized PIB in THF, adding one-half the molar amount of the diisocyanate (Adiprene L-100® of the E. I. DuPont Co.), and allowing the solution to reflux for 20 hrs. The solvent was evaporated and the product was heated in an oil bath to 90°C for 14 hrs. The molecular weight was determined by G.P.C.

^{1}H-NMR spectra were obtained by the use of a Varian T-60 spectrophotometer at room temperature. A Perkin-Elmer 521 infrared spectrophotometer was used.

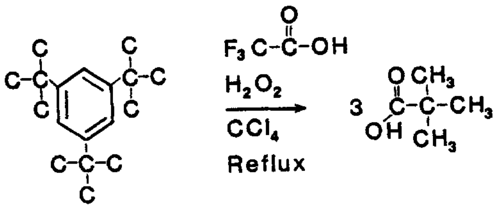
Results and Discussion

As discussed in the introduction a search was undertaken to find a method for the selective degradation of aromatic rings in the presence of aliphatic polymers. A thorough literature survey suggested a number of possibilities among which several have been examined to some depth. For example, the selective oxidation of aromatics by RuO_4 (BERKOWITZ et al., 1958) appeared promising, however, a quantitative selective method could not be developed in spite of extended and detailed investigations (ROSS 1981). Contrary to claims in the literature (GUIZARD and CHERADAME 1979), we found that RuO_4 under a wide variety of conditions degrades not only unsaturated but also aliphatic chains i.e. polyisobutylene (ROSS 1981).

After considerable experimentation we determined that CF_3COOH-H_2O_2 mixtures are eminently suitable for the selective and quantitative oxidative degradation of phenyl rings substituted by polyisobutylene branches. Oxidative cleavage of aromatic compounds by CF_3COOH-H_2O_2 mixtures has been described by DENO et al. 1977. Although the detailed mechanism of this degradation has not been elucidated, it appears that oxidation commences by ring hydroxylation followed by further oxidation, and ultimately leads to ring cleavage yielding chiefly carboxylic acid groups.

<u>Model Experiments</u>

The cleaving of aromatic rings in polymers I and II was investigated by model experiments using a low molecular weight model compound. It was demonstrated that the aromatic ring of 1,3,5-tri-<u>t</u>-butyl benzene is completely destroyed with CF_3COOH-H_2O_2 mixtures in refluxing CCl_4 solvent, however, the aliphatic substituents survive the oxidation.



The model compound tri-<u>t</u>-butyl benzene mimicks the polymers I and II in that it possesses a sterically hindered aromatic ring with branched aliphatic side groups. The progress of the degradation could easily be followed by ^1H NMR spectroscopy: The methyl protons of the tri-<u>t</u>-butyl benzene respond at 1.37 ppm and the aromatic protons at 7.18 ppm. The methyl protons of the reaction product, pivalic acid, appear at 1.22 ppm and the aromatic protons disappear completely.

Oxidative Degradation of Polymers

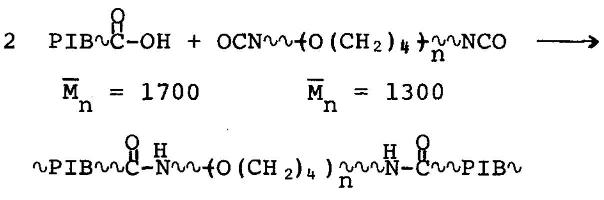
Polyisobutylene

The oxidative degradation of the central aromatic ring of the linear polyisobutylene I and three-arm star polyisobutylene II was carried out under conditions similar to those used with the model compound. Degradation was almost complete after 48 hrs at 60°C i.e., the molecular weight of I decreased to one-half and that of II to one-third of the original value (Figure 1). The molecular weight of the degraded polymers remained constant within experimental error during the next 96 hours. Similarly, the $\bar{M}_n$ of a conventional PIB control (a linear PIB that did not contain aromatic constituents) did not change even after 3 days of exposure to CF_3COOH-H_2O_2 under the same conditions.

Degradative oxidation is quite sluggish at room temperature. Thus the $\bar{M}_n$ of a PIB sample did not change after 24 hrs in the presence of CF_3COOH-H_2O_2 at room temperature. The UV absorbance, however, increased noticeably throughout the distribution (obtained by GPC analysis) which might be due to the formation of hydroxyl or quinone intermediates before ring cleavage.

^1H NMR spectra of the degraded low molecular weight polymers indicated the complete absence of aromatic protons. The degraded products were purified by dissolving them in THF and precipitating into methanol. The IR spectra of these products exhibited an absorption at 1760 cm^{-1} characteristic of the C=O vibration of the carboxylic acid formed.

Additional evidence that carboxylic acid end groups arise from oxidation of the aromatic ring was obtained by coupling the oxidized material with diisocyanate. Thus a telechelic linear PIB ($\bar{M}_n$ = 3400) was oxidized by CF_3COOH-H_2O_2 and the product was subsequently heated in THF solution with a telechelic polyether carrying terminal isocyanate groups of $\bar{M}_n$ = 1300 (Adiprene) at COOH/NCO = 1.0:



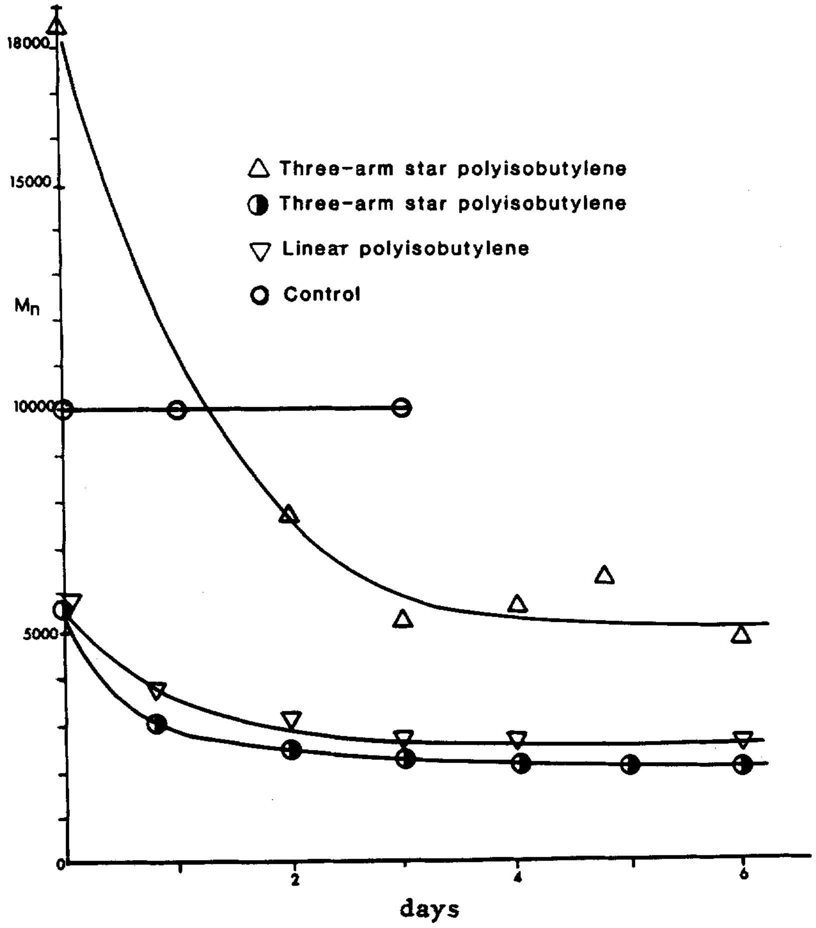
$$2\quad \mathrm{PIB}\sim\overset{\overset{\displaystyle O}{\|}}{C}\text{-OH} + \mathrm{OCN}\sim\sim\!\left(\mathrm{O(CH_2)_4}\right)_n\!\sim\sim\mathrm{NCO} \longrightarrow$$

$$\bar{M}_n = 1700 \qquad\qquad \bar{M}_n = 1300$$

$$\sim\mathrm{PIB}\sim\sim\overset{\overset{\displaystyle O}{\|}}{C}\text{-}\overset{H}{N}\sim\sim\!\left(\mathrm{O(CH_2)_4}\right)_n\!\sim\sim\overset{H}{N}\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\sim\sim\mathrm{PIB}\sim$$

The $\bar{M}_n$ of the product was 4,300, i.e., not far from the theoretical value of 4,700. This discrepancy may be due to the presence of protic impurities in the charge or the fact that the $\bar{M}_n$ of the triblock copolymer was obtained from a GPC calibration curve for PIB.

Figure 1. Molecular Weight Decrease after Oxidative Degradation of the Central Aromatic Ring in Telechelic Polyisobutylenes



Polystyrene

During the course of our investigations it occurred to us that novel heretofore unavailable isobutylene/acrylic acid copolymers could be synthesized by selectively oxidizing with $CF_3COOH-H_2O_2$ the aromatic rings in styrene/isobutylene copolymers. Preliminary experiments in this direction were carried out by oxidizing polystyrene with $CF_3COOH-H_2O_2$ mixtures under conditions described above for polyisobutylenes. The oxidized products did not dissolve in common solvents (CCl_4, n-hexane, dioxane, benzene) and did not melt, however, they swelled in dilute sodium hydroxide. The IR spectrum of a network prepared in this manner was quite similar to that of polyacrylic acid and showed the presence of carboxylic acid groups (1750 cm^{-1}).

Further research will be carried out to exploit the possibilities offered by this selective oxidizing agent.

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References

BERKOWITZ, L. M. and RYLANDER, L. M., J. Am. Chem. Soc. 18, 6682 (1958)
BOESEKEN, J. and ENGELBERTS, R., Koninkl. Akad. Wetensch. Amsterdam Proc., 34, 1292 (1931)
CHAMBERS, R. D., GOGGIN, P. and MUSGRAVE, W. K. L., J. Chem. Soc. 1804 (1959)
DENO, N. C., GREIGGER, B. A., MESSER, L. A., MEYER, M. D. and STROUD, S. G., Tetrahedron Letters, 1703 (1977)
FEHÉRVÁRI, A., KENNEDY, J. P. and TÜDŐS, F., J. Macromol. Sci., Chem., A15 215 (1980)
GUIZARD, C. and CHERADAME, H., Europ. Polym. J. 15, 689 (1979)
IVÁN, B., KENNEDY, J. P. and CHANG, V. S. C., J. Polym. Sci., Polym. Chem. 18 3177 (1980)
KENNEDY, J. P., ROSS, L. R., LACKEY, J. E. and NUYKEN, O., Polymer Bulletin 4, 67, (1981)
KENNEDY, J. P. and SMITH, R. A., J. Polym. Sci., Polym. Chem. Ed. 18 1523 (1980)
ROSS, L. R., Ph.D. Dissertation, The University of Akron 1981

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