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Witold Kuran^a; Jacek Petrus^a

^a Institute of Organic Chemistry and Technology Technical University of Warsaw, Koszykowa, Poland

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Investigations on the Synthesis and Structure of Polymeric Peroxides. Aromatic Polyesters Containing Peroxide Linkages

WITOLD KURAN and JACEK PETRUS

Institute of Organic Chemistry and Technology
Technical University of Warsaw (Politechnika)
00-662 Warszawa, ul. Koszykowa 75, Poland

ABSTRACT

Aromatic polyesters containing peroxide groups incorporated in the polymer chains were synthesized by interfacial polycondensation of bisphenol A, sodium peroxide, and isophthaloyl chloride. Iodometric titration, elemental analysis, and IR spectra showed that the polymers obtained possessed a high peroxide content, even though bisphenol A reacted 80 times faster than Na_2O_2 with isophthaloyl chloride. Analysis of the polymers by high resolution NMR and degradation of the chains with subsequent gel permeation chromatography measurements showed that the distribution of peroxide groups is random in the case of low peroxide content. Higher peroxide content leads to the formation of peroxide blocks in the polymer as well as greater polydispersity of the polyester fragments formed after degradation of the peroxide links.

INTRODUCTION

A method for the preparation of block copolymers by means of radical polymerization of vinyl monomers in the presence of phthalyl peroxide was described in the 1950s [1-3]. By this method, block

copolymers of poly(styrene)-poly(methyl methacrylate) and poly(vinyl acetate)-poly(styrene) were prepared.

Since that time little work has been done in this field. Oligomeric, aliphatic diacyl peroxides, capable of initiating the polymerization of vinyl monomers, have been synthesized [4-7]. Diperoxy and triperoxy compounds containing acyl peroxide and perester groups have also been investigated [8-11]. Such compounds containing two or more peroxide groups in the same molecule decomposing at different temperatures enable the successive polymerization of two vinyl monomers, giving in result a block copolymer.

The present investigation has been undertaken in an attempt to synthesize polymeric peroxides by the condensation of isophthaloyl chloride with 4,4'-(1-methylethylidene)bisphenol (bisphenol A) and sodium peroxide. It was expected that this reaction would yield an aromatic polyester containing acyl peroxide groups, capable of initiating the polymerization of a vinyl monomer and thus enabling the synthesis of a block copolymer.

This work deals with the reaction of isophthaloyl chloride with mixtures of bisphenol A and Na_2O_2 in varying proportions and the characterization of the products obtained, taking into account both the peroxide group content and the distribution of the peroxide groups within the polyester chain.

EXPERIMENTAL

Materials

Technical 4,4'-(1-methylethylidene)bisphenol (bisphenol A) was purified by crystallization from acetic acid/water (1:1) to give white crystals, mp 155-157°C. Sodium peroxide, commercial grade, was analyzed and found to contain 90.1% pure sodium peroxide. An appropriate excess of the compound was used in subsequent reactions. Isophthaloyl chloride was obtained from Fluka AG and distilled under reduced pressure. Triethylbenzylammonium chloride was obtained as described in the literature [12].

Reactions

The reactions were carried out in flasks equipped with a high-speed stirrer, thermometer, and dropping funnel. The appropriate amount of bisphenol A was dissolved in 200 cm³ of an aqueous solution of sodium hydroxide and placed in the reactor. The catalyst (triethylbenzylammonium chloride) and sodium peroxide were also dissolved in 200 cm³ of water and added to the reactor. This reaction mixture was then stirred at high speed while a solution of 0.040 mol of isophthaloyl chloride in 100 cm³ of methylene chloride was added dropwise. The contents of the reactor were stirred for a total of 45 min,

TABLE 1. Composition of the Reaction Mixture for the Interfacial Polycondensation of Bisphenol A, Sodium Peroxide, and Isophthaloyl Chloride in the Presence of Triethylbenzylammonium Chloride (0.002 mol) at Room Temperature

Polymer	Bisphenol A (mol)	Na ₂ O ₂ (mol)	Isophthaloyl chloride (mol)	NaOH (mol)
PP-0	0.040	-	0.040	0.096
PP-5	0.038	0.002	0.040	0.091
PP-10	0.036	0.004	0.040	0.079
PP-20	0.032	0.008	0.040	0.070
PP-50	0.020	0.020	0.040	0.048
PP-75	0.010	0.030	0.040	0.024
PP-100	-	0.040	0.040	-
80/20	0.008	0.032	0.008	0.017
70/30	0.012	0.028	0.008	0.025

then diluted with 400 cm³ of methylene chloride and stirred for another 15 min. Finally, the reaction mixture was acidified to pH 1 with dilute hydrochloric acid. The polymer solution was washed twice with water and the polymer separated by precipitation from methanol, filtration, and drying under reduced pressure. Detailed reaction conditions are given in Table 1.

1,3-Phenylenedicarbonyl/bis[benzoyl peroxide] (I) was synthesized from a freshly prepared aqueous solution of the sodium salt of benzenecarboperoxic acid [13] and isophthaloyl chloride. A solution of 3 g of isophthaloyl chloride in 25 cm³ of CH₂Cl₂ was shaken with an excess of the sodium perbenzoate solution, giving 5.25 g of I. The freshly prepared product was found to contain 94-98% peroxide calculated as C₂₂H₁₄O₈.

Polymer Characterization

The peroxide content of the polymers was determined by the iodometric method using 1,1,2,2-tetrachloroethane/acetic acid (1:1) as a solvent. All determinations were carried out against a blank. Viscosity measurements were carried out in 1,1,2,2-tetrachloroethane at 25°C with an Ubbelohde viscometer.

NMR spectra were recorded on a Jeol JNM 4H 100 spectrometer using TMS as an internal standard and 1,1,2,2-tetrachloroethane as a solvent. IR spectra were obtained from KBr pellets on a Zeiss UR-10 spectrometer.

Degradation of the peroxide bonds in PP-5 and PP-10 was achieved by dissolving 2 g of the polymer in 50 cm³ of 1,1,2,2-tetrachloroethane/acetic acid (1:1) and stirring with 10 cm³ of 40% KI_{aq} for 2 h.

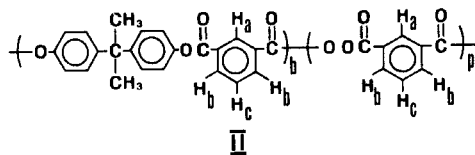
The mixture was then acidified, washed with water, and the resulting polymer separated from the organic phase by precipitation in methanol.

Molecular weight distributions were obtained by gel permeation chromatography on a Waters 202 gel chromatograph equipped with a set of seven columns (Styragel polystyrene gel, pore size 60, 100, 250, 500, 10³, 10⁴, and 10⁵ Å) and differential refractometer detection in chloroform. Number-average molecular weight was calculated on the basis of calibration curves established with standard, mono-disperse polystyrene samples.

RESULTS AND DISCUSSION

Reaction and Polymer Characterization

The interfacial polycondensation of isophthaloyl chloride, bisphenol A, and Na₂O₂ in the presence of triethylbenzylammonium chloride was investigated for various reactant molar ratios. The yield, peroxide content, and intrinsic viscosity of the polymers obtained (II) are presented in Table 2.



The composition of II was calculated on the basis of the peroxide content given in Table 2 and compared with results obtained from elemental analysis (Table 3).

The IR spectra of II are presented in Fig. 1. The C=O absorption band at 1745 cm⁻¹ corresponds to the ester carbonyl group whereas the peroxide C=O groups give absorption bands at 1770 and 1795 cm⁻¹. The relative intensity of the peroxide C=O absorption band increases together with increasing peroxide content of polymer II.

The solubility of II was also investigated. Samples PP-0 through PP-75 were all well soluble in 1,1,2,2-tetrachloroethane and poorly soluble in chloroform, whereas PP-100 was completely insoluble in all solvents.

The above data proves that II is a copolymer with a composition similar to that of the initial reaction mixture. Such a composition is

TABLE 2. Characterization of Polymer II

Polymer II	Yield (%)	Peroxide content (molar fraction) ^a	$[\eta]$ (100 cm ³ /g)
PP-0	86.2	-	1.19
PP-5	97.5	0.047	0.64
PP-10	87.4	0.070	0.68
PP-20	97.9	0.166	1.11
PP-50	91.0	0.447	0.55
PP-75	91.6	0.682	0.28
PP-100	~ 80	-	-
80/20	50.6	0.054	-
70/30	71.0	0.024	-

^aCalculated in relation to isophthaloyl chloride content in the feed.

TABLE 3. Results of Elemental Analysis of Polymer II

Polymer II	Calculated for II ^a		Found	
	C	H	C	H
PP-5	76.70	4.97	75.63	5.00
PP-10	76.44	4.94	75.73	5.05
PP-20	75.49	4.81	74.42	4.86
PP-50	72.21	4.30	71.42	4.44
PP-75	67.87	3.74	66.72	3.92

obtained in the case of equimolar amounts of bisphenol A + sodium peroxide and isophthaloyl chloride. However, in the case of a large excess of bisphenol A and sodium peroxide relative to isophthaloyl chloride (Polymers 80/20 and 70/30, Table 1), the peroxide group content of the polymers formed is much lower than the sodium peroxide content of the initial reaction mixture. The difference in the composition of the copolymer and the initial reaction mixture was used according to Korshak [14] to evaluate the ratio of the reaction rate of sodium peroxide with isophthaloyl chloride (k_1) to the reaction rate of bisphenol A with isophthaloyl chloride (k_2). The ratio k_1/k_2 was found to equal 0.012.

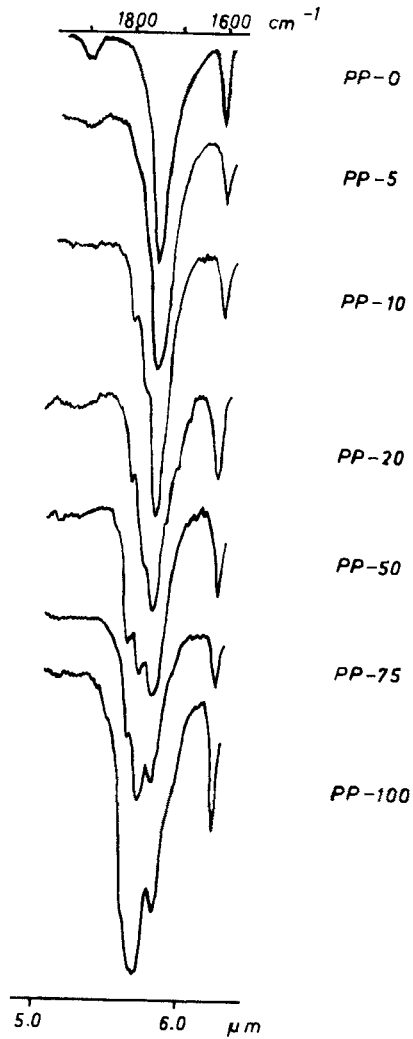
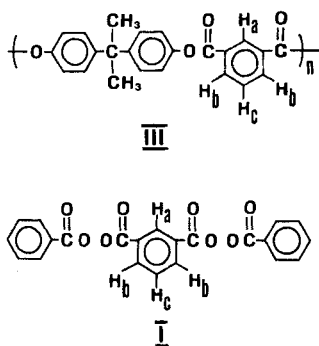


FIG. 1. IR spectra of III (PP-0) and II (PP-5 through PP-100), KBr pellets.

Peroxide Group Distribution

The chain of Polymer II is composed of three structural units, -B-, -I- and -P-, which designate the bisphenol A, isophthaloyl chloride, and peroxide residues, respectively. In order to investigate the distribution of these units in the polymer chain, an analysis of the NMR spectra of II was carried out. The polyester III and (1,3-phenylene-dicarbonyl)bis[benzoyl peroxide] (I) were also analyzed.



The results are presented in Fig. 2 and Table 4. The signal of the H_a proton in II is split into three separate signals. By comparing the chemical shifts of these three signals with the chemical shifts for the H_a proton in III and I, the triads B-I-B, B-I-P, and P-I-P were assigned to signals 1, 2, and 3, respectively. Signal 2 comes from structure B-I-P and therefore the intensity of this peak represents the amount of heterolinkage in Polymer II.

Molar fractions of the B-I-B, B-I-P, and P-I-P triads are obtained from the three kinds of signals in the NMR spectrum. These in turn are used to calculate the degree of randomness (B) and the number-average sequence length of B and P units (\bar{L}_{nB} and \bar{L}_{nP}) according to the method presented by Yamodera and Murano [15]. The results are presented in Table 5. The value of $B = 1.06$ for PP-5 points to the practically random structure of this polymer in which the peroxide groups follow a statistical distribution. The number-average sequence length of peroxide units is equal to 1, which shows that all the peroxide groups are separated from each other in the polymer chains. Together with an increase in the peroxide content of II, the value of B decreases and the value of \bar{L}_{nP} increases, indicating the presence of blocks of peroxide units.

In order to investigate the polydispersity of the polyester chains formed after decomposition of the peroxide groups, II was subjected to degradation using potassium iodide for the reduction of the peroxide

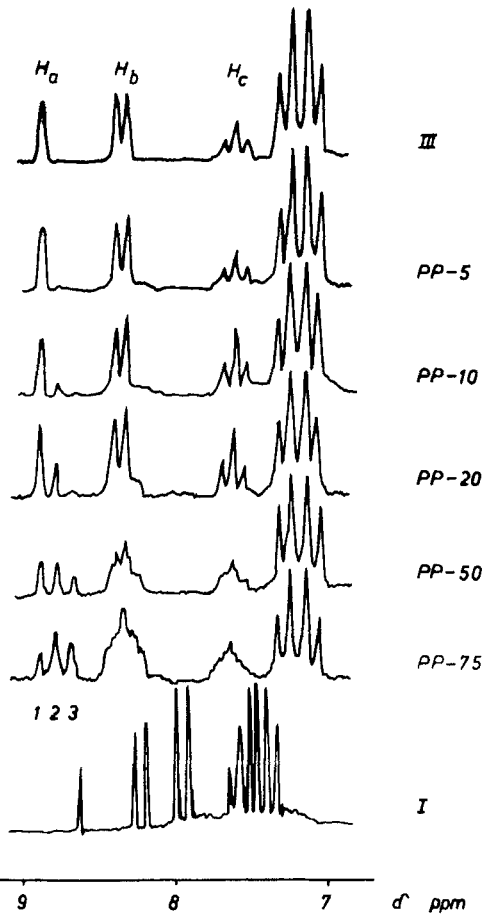


FIG. 2. NMR spectra of III, II (PP-5 through PP-75), and I in 1,2,2-tetrachloroethane solution, room temperature.

TABLE 4. Chemical Shifts and Relative Intensities of the H_a Signal^a in I, II, and III

Sample	Signal ^a	Position of signal (ppm, negative scale)	Relative intensity (%)
III	1	8.96	100
PP-5	1	8.96	87.5
	2	8.87	12.5
	1	8.97	80.9
PP-10	2	8.86	16.7
	3	8.76	2.4
	1	8.96	70.2
PP-20	2	8.85	25.2
	3	8.76	4.6
	1	8.96	42.5
PP-50	2	8.86	38.8
	3	8.75	18.7
	1	8.96	27.5
PP-75	2	8.86	38.2
	3	8.75	34.3
	1	8.96	27.5
I	3	8.68	100

^aSee Fig. 2.TABLE 5. Degree of Randomness (B) and Average Sequence Length of Bisphenol (\bar{L}_{nB}) and Peroxide (\bar{L}_{nP}) Blocks in Polymer II

Polymer II	B	\bar{L}_{nB}	\bar{L}_{nP}
PP-5	1.06	15.0	1.0
PP-10	0.87	10.7	1.3
PP-20	0.88	6.6	1.4
PP-50	0.82	3.2	2.0
PP-75	0.77	2.4	2.8

TABLE 6. Polydispersity of Polyester IV Formed by the Degradation of II

Polymer II	\bar{M}_n	\bar{M}_w/\bar{M}_n
PP-5	1180	2.8
PP-20	840	4.8

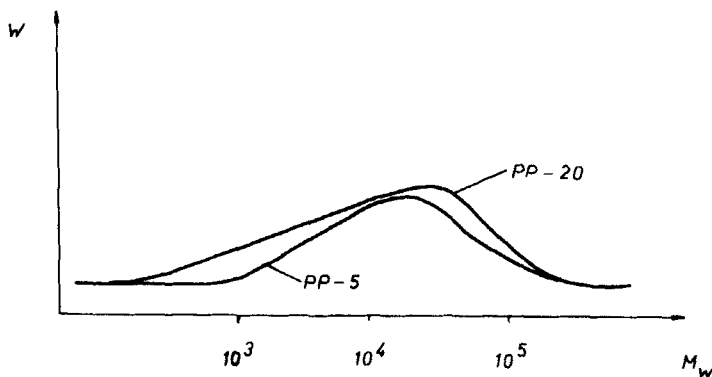
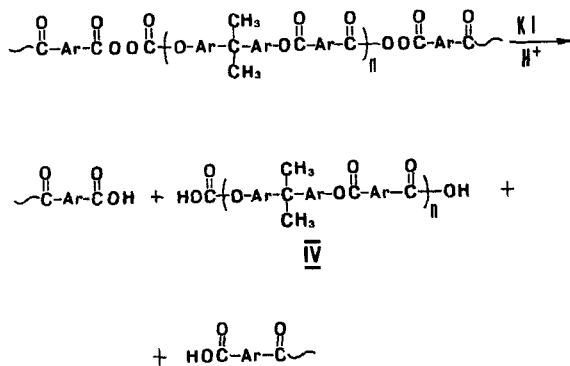


FIG. 3. GPC curves for polyester IV obtained from PP-5 and PP-20 by reduction of the peroxide bonds with KI.

groups. As a result, polyesters IV with terminal carboxyl groups were obtained according to



Polyesters IV were investigated by gel permeation chromatography. Investigations were carried out for Samples PP-5 and PP-20. The

results are presented in Table 6 and Fig. 3. An increase in the peroxide content of II is accompanied by a decrease in the number-average molecular weight of IV together with an increase of its polydispersity, expressed as $\overline{M}_w/\overline{M}_n$.

In conclusion, it may be stated that in the interfacial polycondensation of bisphenol A, sodium peroxide, and isophthaloyl chloride, bisphenol A is the more reactive species but the polymers obtained have a high peroxide group content. In the case of a small sodium peroxide/bisphenol A ratio in the feed, the distribution of peroxide groups in the polymer is random. Together with an increase of this ratio, more block copolymer is formed.

Preliminary investigation of the polymerization of vinyl monomers in the presence of polyesters containing peroxide groups has shown that these polymers initiate vinyl polymerization. Detailed results shall be published at a later date.

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