

SYNTHESIS AND PROPERTIES OF POLYMERS CONTAINING PHOSPHORUS AND NITROGEN*

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The free radical copolymerization of bis-(diethylphosphono)butadiene-1,3 with maleimides has been investigated. The kinetics of the copolymerization reaction were studied and the reactivity ratios of the monomers determined. It is shown that the reactivity of maleimides toward the phosphorus containing macroradical increases as the electronegativity of the substituent on the nitrogen atom increases. Correlation was found between the relative reactivity of the imides and the Hammett and Taft induction constants. The physical heat resistance and thermal stability of the polymers were studied.

POLYMERS and copolymers based on maleimides have high heat resistance, and resistance to various oxidizing agents and radiation [1]. It is known also that when P and N atoms are present simultaneously in a polymer they exert a synergistic effect in raising the fire resistance of the material [2]. For this reason the production of polymers containing phosphorus and nitrogen, and study of their properties, is of definite interest.

In the present paper we report an investigation of free-radical copolymerization of 2,3-bis-(diethylphosphono)butadiene-1,3 (I) with N-substituted maleimides (II) and study of the physical and chemical heat resistance of the polymers. The imides used were maleimide (IIa), ethylol- (IIb), chloromethyl- (IIc), phenyl- (IIId), *p*-methoxyphenyl- (IIe) and *p*-chlorophenylmaleimide (IIf).

The synthesis of I, the purification of the solvents and benzoyl peroxide (BPO) and the copolymerization method were as in reference [3]. The imides II were prepared and purified as described in references [4-7]. The physicochemical constants of the monomers were in agreement with the literature.

Copolymerization as carried out in solution in DMF or dioxan, in the presence of 1% by weight (calculated on monomer) of BPO at 70°. The copolymers were purified by precipitation in diethyl ether. The authenticity and uniformity of the copolymers was proved by fractionation and establishment of the identity of composition of the fractions. The composition of the copolymers was determined from their phosphorus and nitrogen con-

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tents, satisfactory agreement being obtained between the results of microanalysis for these two elements. Preliminary experiments showed that the reactivity of the monomers is not affected by the nature or quantity of the solvents used.

Thermomechanical curves were plotted in an apparatus with automatic recording [8], with a constant load acting on the specimen. The thermal stability of the copolymers was determined from dynamic DTA and TGA measurements. The experimental conditions consisted in heating samples of weight 0.04–0.05 g at a rate of 4.5 deg/min, in air or in a current of nitrogen (flow rate 300–350 ml/min). The chemical change in the solid residues was followed by IR-spectroscopy. The test specimens were obtained by moulding under pressure into pellets with KBr. The volatile degradation products were determined by GLC analysis in a "Khrom-41" apparatus with a katharometer as detector.

TABLE 1. COPOLYMERIZATION CONSTANTS OF I (M_1) AND II (M_2) IN DMF AT 70°

M_2	r_1	r_2	$r_1 r_2$	$1/r_1$
IIa	0.14 ± 0.03	0.43 ± 0.02	0.06	7.1
IIb	0.12 ± 0.03	0.49 ± 0.03	0.06	8.3
IIc	0.05 ± 0.05	0.30 ± 0.05	0.015	20.0
IId	0.05 ± 0.02	0.42 ± 0.07	0.02	20.0
IIe	0.04 ± 0.01	0.47 ± 0.01	0.02	25.0
IIf	0.03 ± 0.01	0.41 ± 0.05	0.01	33.3

The kinetics of copolymerization of I with IIa are described by the usual equation of radical polymerization. The reaction rate is directly proportional to monomer concentration and proportional to the square root of the initiator concentration, indicating bimolecular termination of the polymer chain and the fact that no degenerate chain transfer occurs. The apparent energy of activation for copolymerization in the temperature range of 60–80° is 18.3 kcal/mole.

As a quantitative measure of the reactivity of the monomers in copolymerization, the copolymerization constants of the monomers were found from the dependence of copolymer composition on the initial composition of the monomer mixture, according to the integral equation of Mayo and Lewis [9] (the degree of conversion in the experiments was 20%) (Table 1).

It is seen from Table 1 that in all the systems the reactivity ratios are less than unity and $r_1 r_2 \ll 1$, i.e. the comonomers show a strong tendency to form alternating copolymers.

The relative reactivity of alkylmaleimides toward the polymeric radical I ($1/r_1$) varies according to Taft's equation, $\log 1/r_1 = 0.8 \sigma^* + 0.47$, with the reaction constant $\rho^* = 0.8$ (Fig. 1, curve *a*). The fact that the relationship is linear shows that the substituent does not cause any steric effect, but the relatively high value of ρ^* indicates that the substituents exert a strong polar effect in alkylmaleimides.

There is no clear relationship between the reactivity of the arylmaleimides

and Hammet's constant, evidently because of the considerable distance between the substituent and the reaction centre. The latter fact reduces the effect of polar factors and increases the role of the resonance component. There is good agreement between the reactivity of the arylmaleimides and the modified Hammet equation [10], $\log 1/r_1 = \rho\sigma + \gamma E_r$, where σ and E_r the induction and resonance constants of the substituents, and ρ and γ , the reaction constants, characterize the sensitivity of the polar and resonance effects of the substituents respectively.

TABLE 2. DEPENDENCE OF T_g OF COPOLYMERS OF I WITH II ON COMPOSITION AND ON THE CONDITIONS OF PREPARATION

Composition of copolymers, mole %				T_g , °C (calc. as in [17] and [18])		T_g , °C (experimental)	
I	IIa	IIc	IIId	without H-bonds	allowing for H-bonds	series A	series B
20	80	—	—	144	235	120	190
30	70	—	—	91	147	82	150
50	50	—	—	32	57	35	93
50	—	50	—	68	—	78	90
20	—	—	80	180	—	160	180

The equation of the correlation graph (Fig. 1, curve *b*) takes the form $\log 1/r_1 = 0.27\sigma + 1.5 E_r + 1.3$. Hence both inductive and resonance effects influence the reactivity of the monomers.

Note that polar and resonance effects have been found to be operative in copolymerization of *para*-substituted phenyl methacrylates [11] and phenyl vinyl ketones [12], which have similar values of ρ (0.21 and 0.34 respectively).

The positive values of the reaction constants ρ^* and ρ show that the relative reactivity of maleimides toward macroradical I increases as the electronegativity of the substituent on the nitrogen atom increases, as is the case with alkyl acrylates [13] and other monomers [14–16].

Copolymers of I with the imides II are white powders with good solubility in DMF and dioxan, but are insoluble in acetone, CCl_4 , chloroform and water. Their self extinguishing tendency when withdrawn from a flame is good.

The glass temperature of copolymers with IIa and IIId falls almost linearly as the proportion of phosphorus-containing monomer is increased (~ 4 deg/mole of I).

It was found that T_g of copolymers of I with monomers II is strongly dependent on their prehistory. The properties of two series of copolymers were compared. In one series they were obtained by precipitation from solution by addition of a precipitant (series A), and cast as films from solution in DMF, which is a "good" solvent for these copolymers (series B). The information presented in Table 2 indicates that the difference in T_g between these two series can be as much as 60–70°. Further experiment showed that this difference is

explained not by difference in the state of aggregation of the samples (powder or film), but by the conditions under which the molecular structure is formed. This was shown by the fact that the difference remained when samples of series B were ground to a powder.

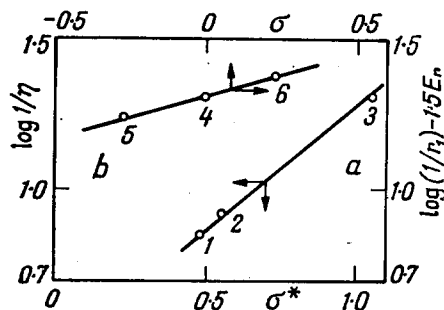


FIG. 1

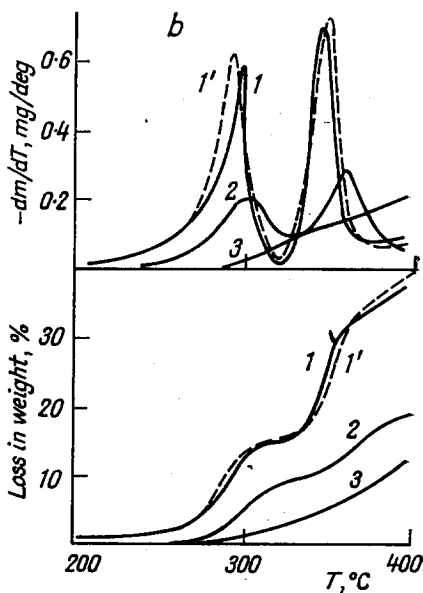


FIG. 2

FIG. 1. Dependence of the relative reactivity of maleimides toward the macroradical I, on the Hammett and Taft induction constants: 1—IIa; 2—IIb; 3—IIc—; 4—IIId; 5—IIe; 6—IIIf.

FIG. 2. Integral (a) and differential (b) weight-loss curves of copolymers of: I with 72.5 wt.% of IIa (1, 1') and 69.5 wt.% of IIId (2), and of butadiene with 50 wt.% of IIa (3); 1–3—in an inert atmosphere, 1'—in air.

It can obviously be considered that these results reflect the relationship that exists between the conformational state of the macromolecules in solution and the extent of intermolecular interaction in the condensed phase. When the polymers are precipitated from solution by addition of a precipitant the globular form of the macromolecules is usually obtained, which in the case of copolymers of I with IIa must cause reduction in intermolecular interaction as a result of screening of groups capable of forming hydrogen bonds with one another, namely $>\text{NH}$, $>\text{C}=\text{O}$ and $>\text{P}=\text{O}$ (series A). The conditions of formation of structure in series B favour uncoiling of the macromolecules, which obviously increases the number of intermolecular contacts in the condensed state of the polymer. This view is confirmed to some extent by the results of calculation of T_g of the copolymers by the universal scheme of calculation [17] (the increments for the phosphorus atom found in reference [18] were used), with (series B) and without

(series A) taking account of hydrogen bonding in the intermolecular interaction. These results are shown in Table 2. It is seen that only when account is taken of the true state (the presence or absence of intermolecular hydrogen bonds) is there a certain correspondence between the experimental and calculated figures.

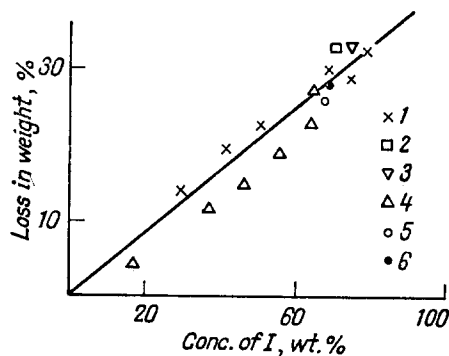


FIG. 3

FIG. 3. Dependence of the weight loss in the first stage of thermal degradation, on the concentration of I in copolymers with: 1—IIa; 2—IIb; 3—IIc; 4—IId; 5—IIf; 6—IIg.

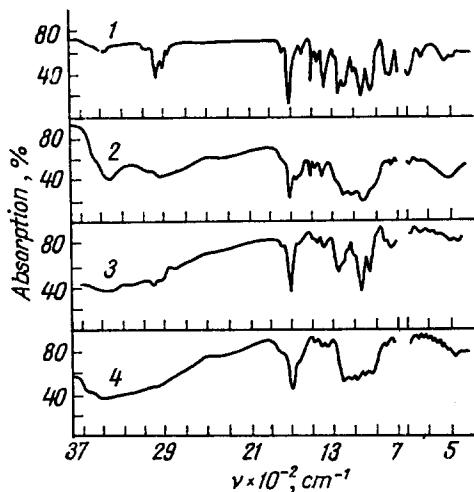


FIG. 4

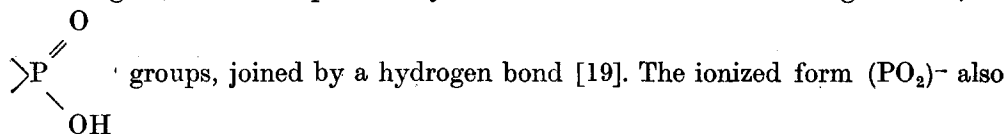
FIG. 4. IR-Spectra of untreated copolymers with IIa (1) and IId (2), and after heat treatment in argon under a routine of gradual rise in temperature, at the end of the first degradation stage (3, 4).

In the case of N-substituted maleimides where intermolecular hydrogen bonding is impossible, the conditions of preparation of the samples do not play such an important part, as would be expected, and the measured difference in T_g is not more than 10–20°.

Both thermal and thermal-oxidative degradation of copolymers of I with IIa and IId occurs in two stages in the temperature range of 200–400° (Fig. 2). In the first stage (250–320°), which is endothermic, there is a certain correspondence between loss in weight toward the end of the stage, and the concentration of phosphorus containing units in the copolymer (Fig. 3). This fact and the single stage and exothermal nature of the degradation in this temperature range of copolymers of butadiene with IIa (specially prepared for comparison) (Fig. 2, curve 2), indicate that phosphorus containing groupings are predominantly involved in decomposition in the first stage.

The structural changes that occur in thermal-oxidative degradation of the topolymers are reflected in the IR spectra (Fig. 4). The marked weakening of the $\nu_{P=O}$ band at 1240 cm^{-1} and the occurrence of absorption in the 1140–1190

cm^{-1} region, can be explained by formation in the course of degradation, of



absorbs in this region [20]. The spectra of samples heated to the end of the first stage, also show other signs of the P—OH group, namely a broad band in the 2200–2700 cm^{-1} region and an overtone at 1640 cm^{-1} . New bands in the 1000–1010 cm^{-1} and 930–940 cm^{-1} regions are evidently attributable to the valency vibrations of P—(O)H and $\begin{array}{c} \parallel \quad \parallel \\ >\text{P}-\text{O}-\text{P}< \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$ groupings [20].

Analysis of the gas phase when a I/IIa copolymer (containing 77.3% by weight of I) is heated under gradually rising temperature conditions to 285° in a vessel evacuated to 5×10^{-3} torr, showed the presence of ethylene (the main component) and some carbon dioxide ($\sim 5\%$).

After completion of the first stage of degradation it was noted that the residue had gained in phosphorus content (Table 3).

The combination of results reported above, indicate that the main source of loss in weight in the initial stage is dealkylation of phosphonate groups and subsequent dehydration of the resulting P—OH groups. It is possible that this produces $\text{R}-[\text{PO}_2^-]$ or $\begin{array}{c} \parallel \quad \parallel \\ >\text{P}-\text{O}-\text{P}< \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$ groupings [2, 22]

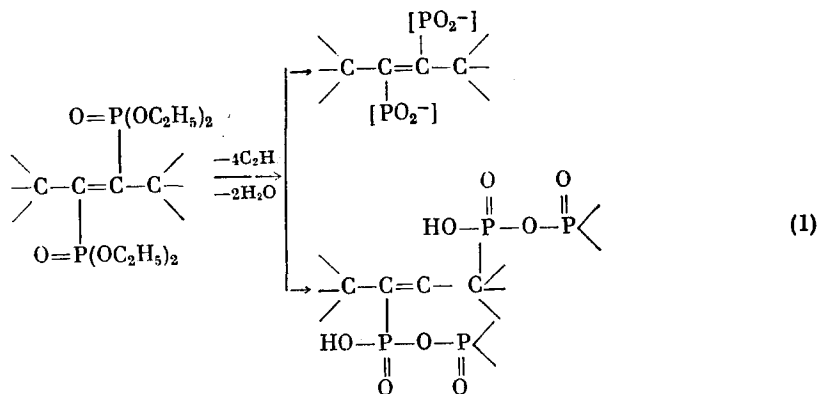
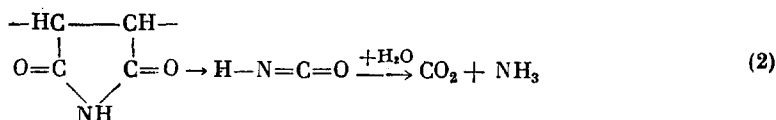


Figure 3 shows the relationship between the loss in weight and the concentration of I in the copolymer, calculated according to the proposed scheme of decomposition (1) (continuous line), and Table 3 shows the phosphorus content of the residue. It is seen that scheme (1) is not completely realized.

It is evident that in the case of copolymers of I with IIa, partial degradation of imide units forms an additional source of loss in weight. This is supported by the fact that carbon dioxide is evolved, formed probably by reaction of the

isocyanate products of decomposition of imide units [23], with the water liberated by dehydration of P—OH groups



The lower loss in weight of copolymers of I with II_d, than the calculated loss, is probably due to steric hindrance to formation of pyrophosphate linkages.

TABLE 3. PHOSPHORUS CONTENT OF COPOLYMERS OF I WITH II

Composition of copolymers, mole %			P, %		
I	II _a	II _d	initial	at end of stage	calc. accord- ing to scheme (1)
50	50	—	14.7	16.7	21.4
49	—	51	12.2	12.9	16.8

Calculation of the kinetic characteristics of degradation by the method of reference [24], gave satisfactory results only in the case of copolymers of I with II_d. The first stage is described by a kinetic equation of the first order, the values of the apparent energy of activation E_a being dependent on the concentration of I and varying within the range of 37.4–42.7 kcal/mole. Values of E_a similar to these have been found in the case of copolymers of vinyl phosphonates with ethylene [21].

Note that replacement of the imide hydrogen in II_a by CH₂OH or CH₂Cl groups, or introduction of substituents such as OCH₃ or Cl in the *para*-position of the benzene ring of II_d, does not affect the loss in weight substantially in the first stage of degradation (Fig. 3).

The second stage of degradation of the copolymers (340–400°) is exothermic regardless of the nature of the gaseous medium. The IR spectra of the residues of copolymers of I with II_d, heated above 320° by a gradually rising temperature routine, show a marked reduction in the intensity of the $\nu_{\text{C=O}}$ bands at 1710 and 1780 cm⁻¹, of the amide band at 1390 cm⁻¹ and of a number of bands characteristic of a monosubstituted benzene ring (700, 760, 1500 and 1600 cm⁻¹), i.e. at this stage vigorous decomposition of imide units occurs, and in air oxidative degradation of diene fragments is also possible.

Thus by copolymerization of 2,3-bis-(diethylphosphono)butadiene-1,3 with maleimides, it is possible to obtain polymers containing phosphorus and nitrogen, with reduced flammability and with resistance to heat up to 250°, which indicates the possibility of using them as fire retarding agents in polymeric materials.

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