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NEW WATER-SOLUBLE POLYMERS BASED ON POLYISOBUTYLENE

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ABSTRACT : *New water-soluble polymers on the basis of polyisobutylene have been synthesized. The active groups (dichlorophosphoride) are added to the polymer chain as a result of its treatment by phosphorus trichloride in the presence of oxygen. After the interaction of the reaction product with sodium hydroxide and diethylamine, polymers which contain different functional groups have been obtained. H-NMR and IR-spectra of these polymers have been recorded and thermostability of the modified polymers have investigated by the thermogravimetric analysis method. Sodium-containing polymer has modified by alkyl halides and their surface tension is determined by stalagmometric method.*

KEY WORDS: *Polimerization, water-soluble polymers, polyisobutylene thermogravimetric analysis.*

POLİİSOBUTİLENDEN SENTEZLENEN SUDA ÇÖZÜNEBİLEN YENİ POLİMERLER

ÖZET : *Poliizobutilenden suda çözünebilen yeni polimerler sentezlenmiştir. Polimer zincirine aktif gruplar (diklorofosforik) ilave edilmiş ve bunun sonucu olarak oksijenli ortamda triklor fosfor giderilmiştir. Reaksiyon ürününün sodyum hidroksit ve dietilamin ile etkileşimi sonunda farklı fonksiyonel grupları içeren polimerler elde edilmiştir. Bu polimerlerin H-NMR ve IR spektrumları alınmıştır. Modifiye edilmiş polimerlerin ısı kararlılığı termal gravimetre analiz yöntemiyle incelenmiştir. Sodyum içeren polimerler alkilhalidlerle modifiye edilmiş ve bunların yüzey gerilimleri stalagmometre yöntemiyle saptanmıştır.*

ANAHTAR KELİMELER: *Polimerizasyon, suda çözünen polimerler, poliisobutilen, termal gravimetrik analizler.*

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I. INTRODUCTION

Producing new water-soluble surface-active polymers based on industrially available products is a serious task, since these polymers find a wide application in various fields, including oil industry, of national economy. In this connection, the reaction of oxidative phosphochlorination of synthetic rubber, based on polyisobutylene (PIB), is of primary interest.

Studies of phosphochlorination reactions of oily polyethylene, atactic polypropylene, polyvinyl acetate and others were reported in literature [1-5]. It was indicated that, in the case of polyolefins, this reaction is not accompanied by significant destruction of the main chain [1,6,7].

Present work covers the results of studies on producing water-soluble polymers by phosphochlorination of PIB and further modification by basic and alkyl halide compounds.

II. EXPERIMENTAL METHOD

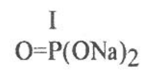
As starting materials the industrially produced "butyl-rubber" (as a model of PIB),oxygen and phosphorus trichloride (PCl_3) were used. Butyl-rubber (molecular mass ~100000) was purified by reprecipitation from n-heptane to isopropanol and was dried in vacuum at 150 ^oC.

Oxygen was dried by concentrated sulphuric acid. For phosphochlorination, the oxygen was passed through a solution (2 % by mass) of rubber in PCl_3 with a rate of 240 ml/min. The temperature during the whole experiment was kept at 165 ^oC (the reaction is slightly exothermic). Depending on the reaction time polymers with different content of phosphorus (up to 16 % mass) were obtained. PCl_3 and phosphorus oxychloride ($POCl_3$) were removed by distillation at low pressure and they were replaced gradually by p-xylene. Thus, phosphodichloride ($-POCl_2$) groups were introduced into the polymer.

III. RESULTS AND DISCUSSION

Due to the interaction of the polymer containing $-POCl_2$ groups, with sodium hydroxide and diethyl amine, products with $-PO(ONa)_2$ and $-PO(N(C_2H_5)_2)_2$ groups were obtained. Solutions of the polymer having $-PO(ONa)_2$ groups were prepared at different concentrations in distilled water and their coefficients of surface tension were measured by stalagmometric method at the water-kerosene interface at 20 ^{o}C (Fig. 1). It should be mentioned that, without addition of polymers, the coefficients of surface tension has got the values in the range 46.5-48.0 erg/cm^2 (at 20 ^{o}C). As seen from Figure 1 the polymers are surface-active.

H-NMR-spectra of the modified polymers which have been registered at "Tesla" spectrometer "BS-487 C" (Chekhoslovakia) are shown in Figure 2. The multiplet at 3.9-4.2 ppm are related to -CH fragment. The signals at 1.5-1.7 ppm may belong to the - CH_2-C- and -C-CH-fragment (Fig. 2a).



$$\begin{array}{c} | \\ O{=}P(ONa)_2 \end{array}$$

The quartet at 3.2 - 3.55 ppm and the triplet at 1.45 - 1.75 ppm are related to -CH_2- methylene, and -CH_3 methyl protons respectively (Fig 2b).

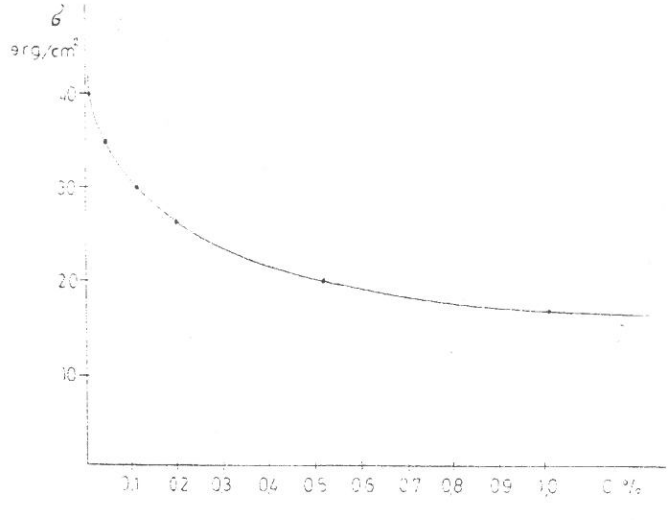


Figure 1. Concentration dependence of surface tension of product solution of the modified PIB (in Na form) at the interface of water-kerosene, at 20 ^{o}C

IR-spectra of the modified polymers have been recorded at spectrometer "UR-20" (Germany). They are illustrated by Figure 3. Bands in between 2800 - 3100 cm^{-1} and 1400 - 1500 cm^{-1} regions are due to -CH-, -CH_2-, -CH_3- groups. Absorbtion at 1150 - 1180 cm^{-1} and 990 cm^{-1} are due to P=O and P-O valence vibrations, and band at 730-

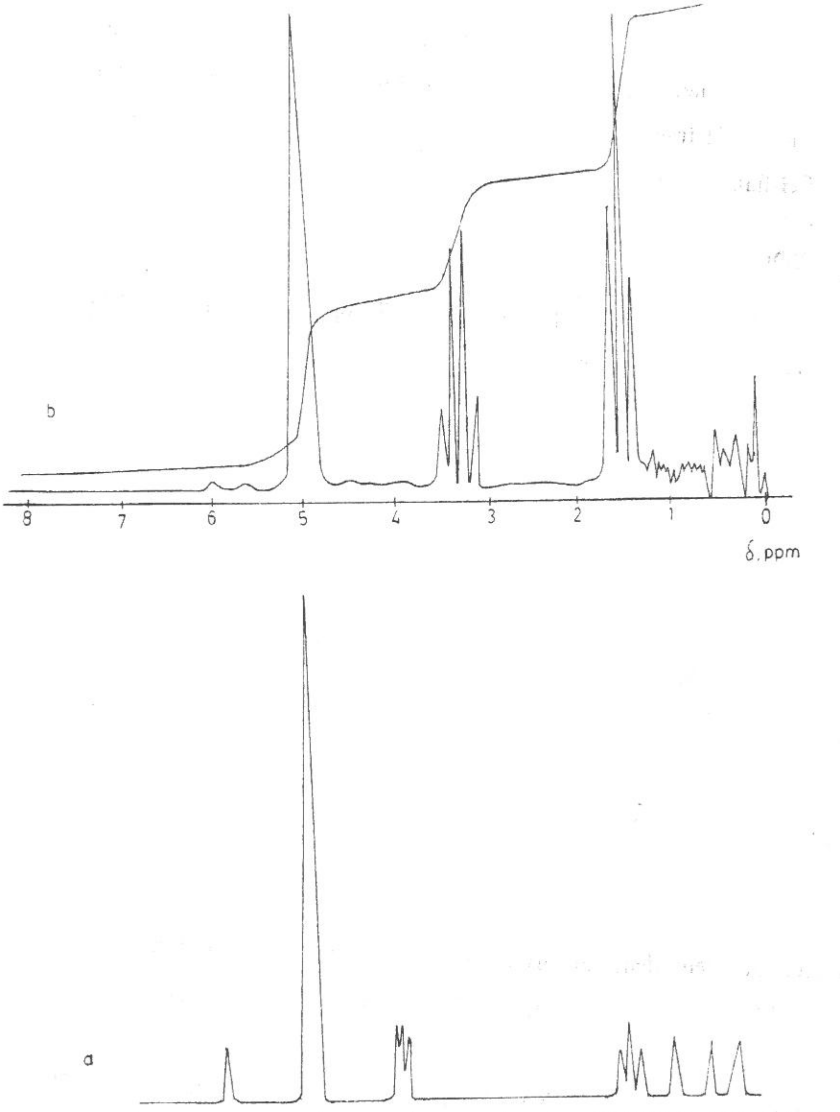
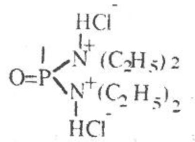


Figure 2. H-NMR-Spectra of the modified polymers a) Modification by NaOH
b) Modification by diethyl amine

750 cm^{-1} is due to deformation vibrations of these bonds (Fig.3a). The broad band at 3350 - 3550 cm^{-1} and at 820 cm^{-1} are due to the valence and deformation bands of the -N-H bond (Fig.3b). The band at 940 cm^{-1} is due to the valence vibration of P-N bond in the molecule:



Thermal stability of the modified polymers was studied by the method of thermogravimetric analysis at the derivatograph "MOM" of the system "Paulic, Paulic

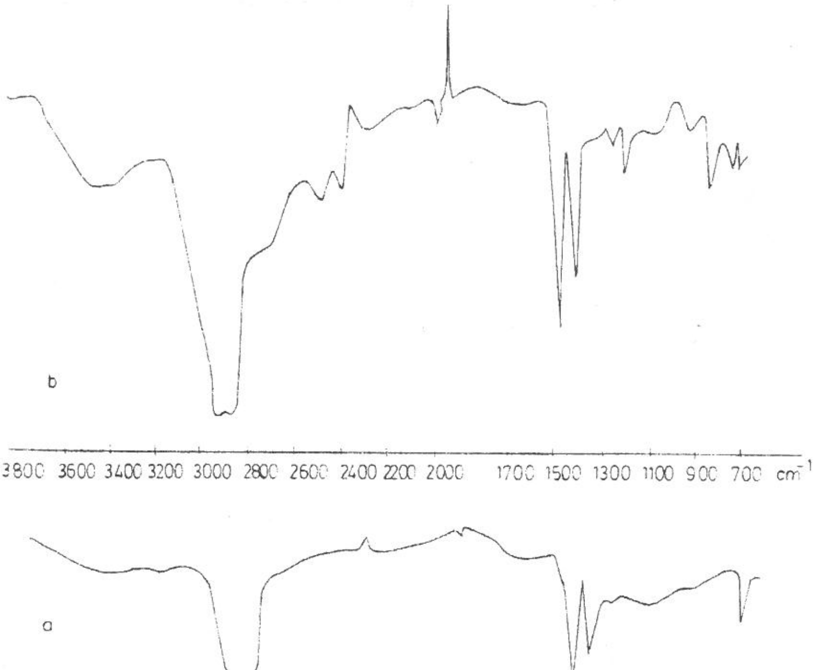
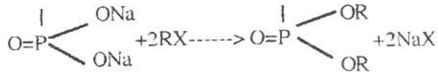


Figure 3. IR-Spectra of the modified polymers a) Modification by NaOH

b) Modification by diethyl amine

and Erdei" (Hungary). As seen from the thermogravimetric curve (Fig.4), the polymer having -PO(ONa)$_2$ groups is of high thermal stability. Up to 170 °C the total loss of mass amounts to 17 %; to 460°C, 20.5 %; and to 620°C, 21 %. Further increase of the temperature to 900 °C does not cause any additional loss of mass.

From Figure 5 it may be seen that the polymer synthesized by modification with diethyl amine has a lower thermal stability. Up to 200 °C the loss of mass was 4 %, to 410 °C 93 % and to 635 °C 95 %. The polymer containing-PO(ONa)$_2$ groups was additionally modified by alkyl halides (CH_3I, C_2H_5I, C_3H_7I, $C_5H_{11}Br$) in order to increase hydrophobicity, due to some extent, to formation of ester groups:



$$O{=}P(ONa)_2 + 2RX \dashrightarrow O{=}P(OR)_2 + 2NaX$$

where R is alkyl radical and X is halogen.

The reaction was conducted at 20°C for 24 hours. The final polymer product was dried to a constant mass.

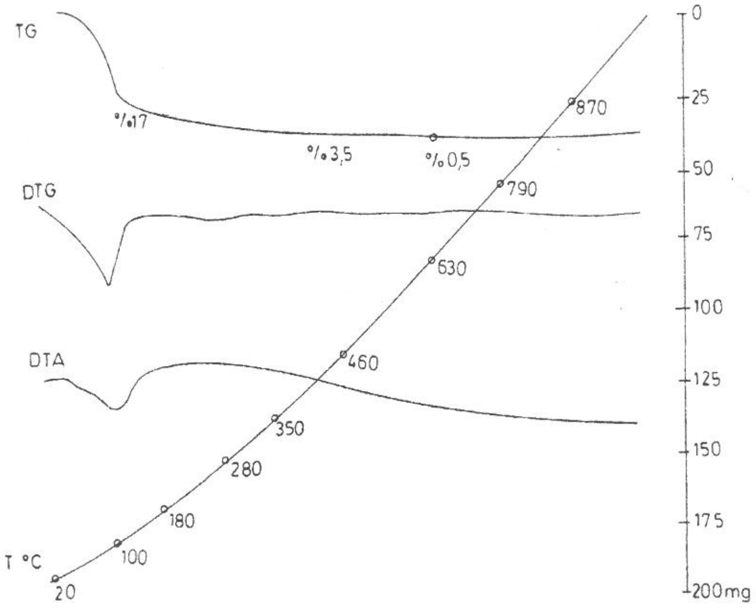


Figure 4. Thermogravimetric curves of the product for modified of PIB (in Na form)

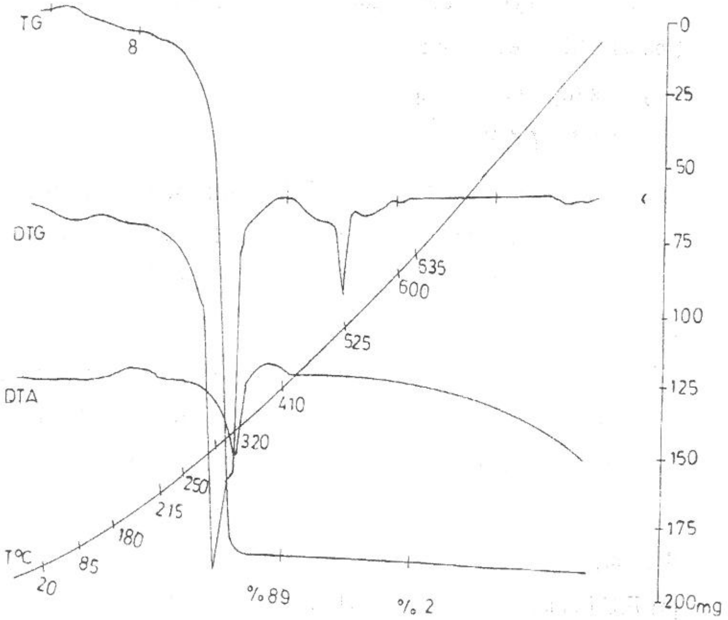


Figure 5. Thermogravimetric curves of the product for modified of PIB by diethyl amine

The results of stalagmometric measurements of the coefficient of surface tension are given in Table 1.

Table 1. Coefficients of surface tension(σ) of the polymers based on PIB and on those modified by PCl_3, NaOH and alkyl halides at the interface of water-kerosene (20°C)

Alkyl halide	σ (erg/cm^2) of the modified polymer	Conversion of the alkyl halide, %
CH_3I	13.46 at C= 0.96 %	75.7
C_3H_7I	10.94 at C= 0.5 %	47.5
	9.87 at C= 2.38 %	
$C_5H_{11}Br$	10.00 at C= 0.58 %	
	8.10 at C= 1.69 %	-

As is evident from the table, the degree of conversion of alkyl halide increases with a decrease of alkyl radical length. It can be explained by the influence of steric factor (spatial difficulties in the case of longer radicals). High surface activity of the synthesized polymers stipulates their application as a surfactant.

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