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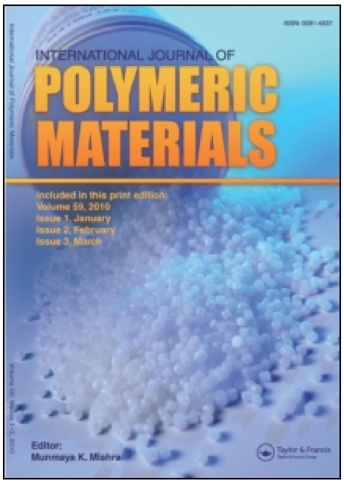

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An IR Study of the Polyethylene and Primary Aromatic Amines Interaction

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The interaction of 4,4′-diamino-3,3′-dichlorophenylmethane and polyethylene with increased amount of unsaturated fragments in polymer chains and also with its low molecular analog-decene-1 was investigated. It was shown that the interaction occurs by both addition to the double bonds and by formation of H-complexes with participation of amino groups and oxo-functions formed in the course of polymer thermo-oxidation. The conclusion is confirmed by the results of quantum-chemical calculations of model systems.

Keywords: Polyethylene; primary aromatic amines; interaction

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INTRODUCTION

It was shown before [1] that incorporation of primary aromatic amines (PAA) into materials based on polyethylene (PE) synthesized by the gas-phase method (PEG) using the chromium-organic catalysts type cilylchromate leads to significant improvement of the polymer-coatings properties. The most significant difference between, PEG, high density PE, suspension liquid-phase low density PE synthesized by Ziegler type catalist, and also PEG of injection molding types synthesized

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by using chromacene type catalists is higher content of unsaturated groups $> C{=}C <$ [2].

We assumed that the interaction between PEG and PAA proceeds by attachment of the primary amino groups to the double bonds in the macromolecular chains of PE with formation of secondary amines:

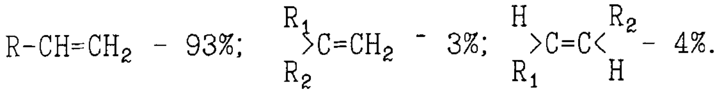
$$Ar{-}NH_2 + H_2C{=}CH{-}R \rightarrow Ar{-}NH{-}CH_2{-}CH_2{-}R$$

and also of formation of hydrogen bonding of the $-NH_2$ groups with the $> C{=}O$, $> C{-}OH$ and $-C{=}O$ groups formed in the course of PE thermo-oxidation. This work is devoted to experimental verification of this assumption.

EXPERIMENTAL PART

Materials

The PEG type 289 with $M_n = 16.000$, $M_w = 280.000$ containing 1.1 double bonds on 1000 carbon atoms of the polymer chain was used. The polymer had the following double bond structure distribution:



$$R{-}CH{=}CH_2 \; - \; 93\%; \quad \overset{R_1}{\underset{R_2}{>}}C{=}CH_2 \; - \; 3\%; \quad \overset{H}{\underset{R_1}{>}}C{=}C\overset{R_2}{\underset{H}{<}} \; - \; 4\%.$$

The films of PEG + 4,4′-diamino-3,3′-dichlorophenylmethane (DX) were prepared by heating the powdered components in an oven heated to 220°C in air and in vacuum (10^{-1} Pa, preliminary gas removal for 1 hrs at 20°C) and also by press molding under pressure of 10 MPa. The extraction of unreacted DX from PEG was conducted by acetone for 96 hrs.

The reaction of DX with decene-1 (mol ratio 1 : 10 correspondingly) was conducted under continuous stirring for 3 hrs. at 170°C. The resin like reaction product was separated from decene-1 by filtration, then it was washed off from the unreacted crystallic powder DX and dried to constant weight over water free $CaCl_2$.

Test Procedures

The IR-spectra were obtained by using the spectrophotometer IR-75, M-80. The PEG containing PAA and the reaction product of DX with decene-1 were tested in films. The DX was tested in a suspension in a vaseline oil. The double bond content in PEG was determined according to procedure published in [3].

Quantum-chemical calculation were performed by using a semi-empirical metod AM1 according to the program MOPAC version 6.0 [4–6]. The calculation were done with full optimization of molecular geometry using IBM PC/486. The metod AM1 is a version of a semi-empirical metod NPD (the zero differential overlapping) which is useful for calculations of systems with hydrogen bonding.

RESULTS AND DISCUSSION

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The IR-spectra of DX absorbtion in the range of 3500–3200 cm^{-1} are shown on Figure 1. It is seen that there are two absorption bands – 3362 cm^{-1} and 3443 cm^{-1} related to symmetrical and asymmetrical valent vibrations of the N—H—link of the $-NH_2$ group ($\nu_s NH_2$ and $\nu_{as} NH_2$) [7, 8]. On the same Figure 1 there are also spectra of DX treated at 220°C in the matrix of PEG both for 5 min. ("low oxidized") and 30 min. ("strongly oxidized" PEG sample). The state of oxidation of the samples was determined by the ratio D_{1720}/D_{1306} [3], where D_{1720} is the optical density of the band $\nu(C{=}O)$; and D_{1306} is the optical density of the deformational vibration band of the CH_2 group which was used as a internal standard for PE. The oxidation state of the "low oxidized" sample was 0.6 and the "strongly oxidized" sample was 2.5. It should be noted that in the indicated range of the PE spectra there is a wide band related the $\nu(-OH)$ [9]. Because of this, the different spectra (DX + PEG) – (PEG) are shown on Figure 1. It is seen that even in the "low oxidized" sample where is noticeable widening of the $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ bands of the IR-spectrum. This allows to assume that there is an interaction between amino groups and PEG molecules.

In case of "strongly oxidized" sample, the widening of corresponding bands are more significant and the absorption increases in the area of lower frequencies (~3280–3200 cm^{-1}). This result gives basis to consider the existence of H-bonding in the system [10] between the $-NH_2$ groups with the oxygen containing groups of PEG. Besides, a new band near 3400 cm^{-1} appears which is absent both in the original

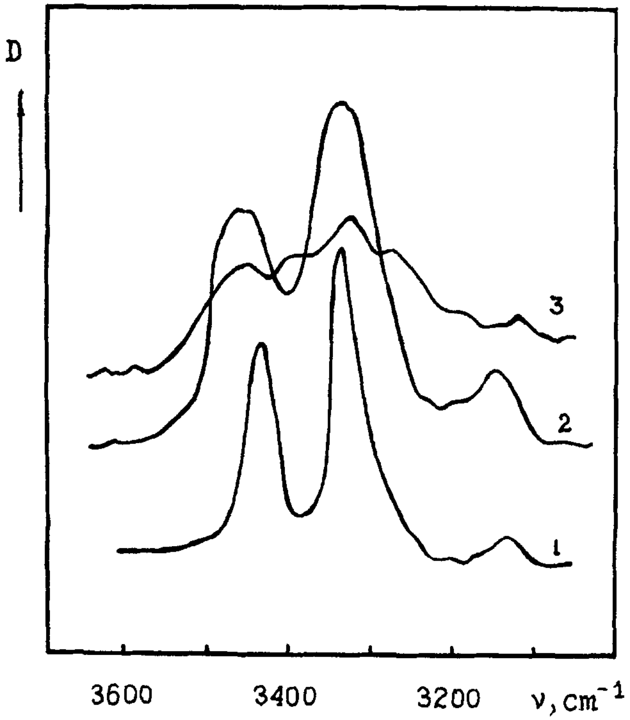

FIGURE 1 IR-spectra of 4,4′-diamine-3,3′-dichlorodiphenylmethane (DX): 1 – original; 2,3-different spectra: (PEG + 2%DX) – (PEG); 2 – heat treated at 220°C for 5 min.; 3 – heat treated at 220°C for 30 min. *D*-optical density.

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DX sample and in the "low oxidized" sample. The band is related to the N—H valent vibration in the second amino group ν(NH) [7, 8]. This indicates the transformation of some primary amino groups into the secondary ones.

To separate the input of chemical interaction and formation of hydrogen bonds into the change of corresponding bands of IR-spectra, the process of heat treatment of samples containing DX was performed in vacuum. This allowed us to minimize the amount of oxygen containing group during the thermooxidation.

The data on Figure 2 show the dependence of the PEG thermooxidation state on DX concentration in samples undergo the heat treatment both in air and in vacuum. The decrease of the $>C=O$

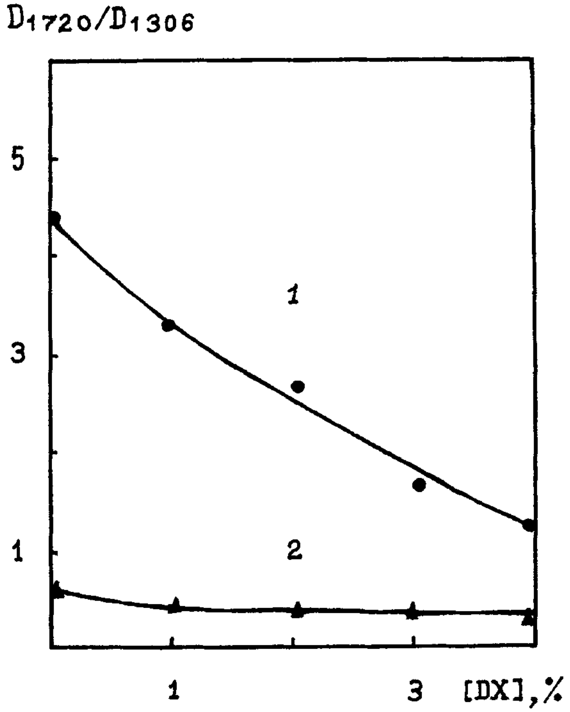

FIGURE 2 Dependence of PEG samples state of heat oxidation on DX concentration: 1 – treated in air; 2 – treated in vacuum.

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group with increase of DX is based on the fact that PAA inhibits the thermooxidation of polymers including PE [1, 11].

The IR-spectra of samples prepared in vacuum are shown in Figure 3. It is seen that the intensity and width of the bands $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ are analogous to the ones obtained for the "low oxidized" sample and the band 3400 cm^{-1} is clearly visible. Additional heating of the "low oxidized" sample at 220°C for 10 min. in the course of PEG press molding gives the same result because the oxygen availability in this case is also limited (see Fig. 4a). The prolonged acetone extraction of the unreacted DX from the heat treated PEG leads to a decrease of the intensity of the bands $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ while the intensity of the ν(NH) retains unchanged (Fig. 4b). Finally, we found a decrease of the vinyline group $R{-}CH{=}CH_2$ concentration in PEG with an increase of the DX content. This can not be

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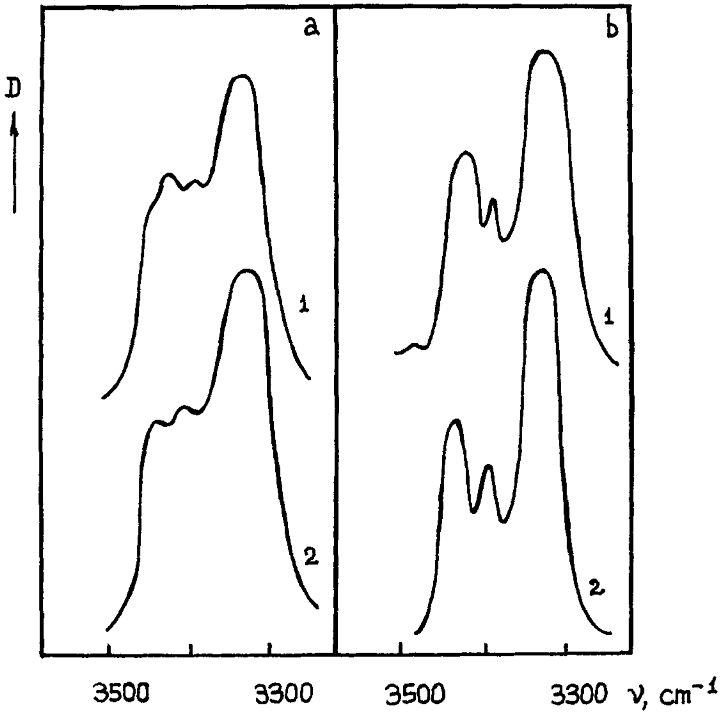
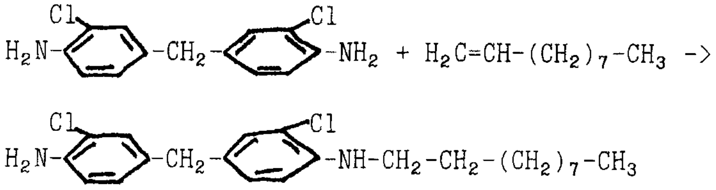


FIGURE 3 IR-spectra of PEG prepared by heat treatment in vacuum and containing DX (mass%): 1) – 2, 2) – 3; a/-original, b/-differential: (DX + PEG) – (PEG).

explained by disappearance of the unsaturated groups in the course of the thermooxidation because DX inhibits this process [1].

The combination of experimental results mentioned above confirms the addition of DX to PEG. For a strict proof of this conclusion we performed a model reaction of DX with decene-1 which can be described as follows:



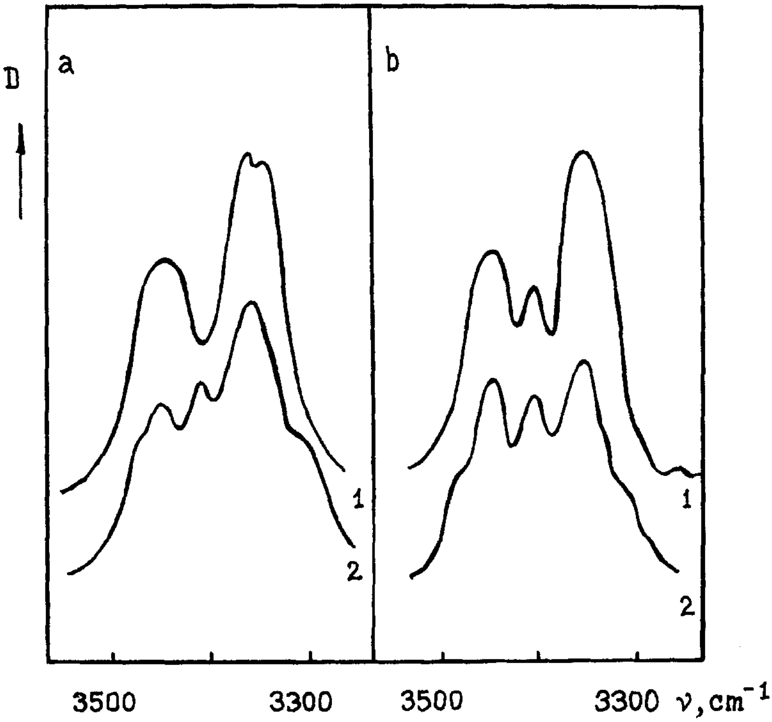


FIGURE 4 IR-spectra of PEG samples containing 2% of DX; a/-low oxidized sample (1); the same sample additionally heat treated in press at 220°C for 10 min. (2); b/-sample prepared in vacuum before (1) and after extraction by acetone to remove unreacted DX (2).

In the IR-spectrum of the resin like reaction product there is a band in the area of $1200\,\mathrm{cm}^{-1}$ which can be related to valent vibrations of the link $C_{\mathrm{aliphatic}}-N$ in the group Ar—NH—R [7, 8] and a band in the area of $1360\,\mathrm{cm}^{-1}$ related to the deformational vibrations of the $-CH_3$ group [3, 9]. Compared with the original DX spectrum, the intensity of the bands in the area of $3000-2800\,\mathrm{cm}^{-1}$ is manyfold increased. These bands are related to $\nu(-CH_3)$ and $\nu(-CH_2)$. An intense duplex appeared in the field of $3600-3100\,\mathrm{cm}^{-1}$ instead of two bands $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$. The duplex is probably a superposition of $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$, $\nu(NH)$ and $\nu(OH)$ of the oxidized carbohydrogen chain (see Fig. 5). Hydrogen bonds between amino and oxygen containing groups are the cause of the widening of the bands.

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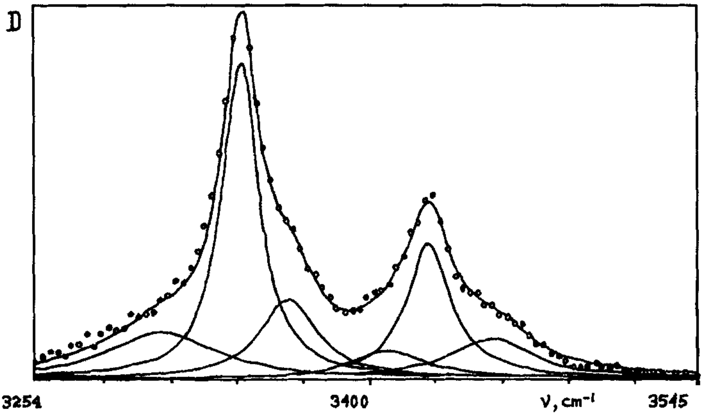


FIGURE 5 IR-spectra of the resinous reaction product of 1-decene with DX. The experimental absorption curve was reduced to individual components. *D*-optical density, *ν*-wave number.

The oxygen containing groups in the reaction product are present based on the existence of the band 1720 cm^{-1} $\nu(C = O)$.

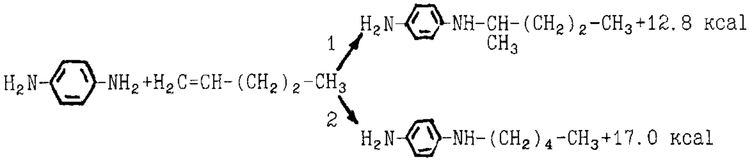
The energies of H-bonding which can be formed between PAA and PEG were evaluated by using the quantum-chemical calculations. The results are shown in Table I. They indicate that the H-bonding energy between nitrogen atoms and the formly hydrogen is very low. However, the values of the hydrogen bonds between amine proton and oxygen of carbonyl group are significantly higher and correlate with published data [10].

Thus, the addition reaction of primary amine group to PEG and decene-1 double bond took place at elevated temperatures. The quantum-chemical calculation of the enthalpy (ΔH) of the reaction leading to formation of C—N bonds according to the Markovnikov

TABLE I Energies of H-bond determined by quantum-chemical calculations using low molecular model compounds

Model compound	*Bond type*	*Bond energy, kJ/mol*
$H_3C—CH_2—CH_2—COH$	$—H_2N\cdots H—CO—$	6.0
$H_3C—CH_2—CH_2—COH$	$—HN—H\cdots O=CH—$	12.0
$H_3C—CO—CH_2—CH_3$	$—HN—H\cdots O=C(CH_3)—$	12.5

rule (way 1) and against (way 2) shows that the nitrogen addition occurs more likely to the chain end carbon:



CONCLUSIONS

The results of IR-analysis and the quantum-chemical calculations show that the interaction between primary aromatic amines and gas-phase polyethylene occurs both by addition of PAA to the unsaturated macromolecular fragments and by formation of H-complexes with participation of amino groups and oxo-functional groups appearing in the course of polymer thermooxidation.

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