trocatalytic properties of electrodes Copolymers of Zn(1,10-phen)(TMHPP)$_2$ and Zn(p-NH$_2$)TTPP show significant enhancement of catalytic process over their constituents. This is especially true for electrocatalytic oxidation of hydrazine and reduction of oxygen directly to water. Generally, electrocatalytic reduction of oxygen is enhanced for all copolymers studied. One of the other important conclusion of these studies is the fact that porphyrinic polymeric and copolymeric materials show high catalytic activity in oxygen reduction even in the absence of coordinated metal.

Registry No. H$_2$(p-NH$_2$), 141509-35-5; H$_2$(p-NHAc), 141509-34-4; Zn(p-NH$_2$)(TMHPP), 141526-70-7; H$_2$(1,10-phen)(TMHPP)$_2$, 141509-36-6; H$_2$(p-pyr)TMHPP, 141509-37-7; Ni(p-pyr)TMHPP, 141526-71-8; H$_2$(p-pyr)TTPP, 141509-38-8; NI[H$_2$(p-pyr)]TTPP, 141526-72-9; H$_2$(1,10-phen)(TMHPP)$_2$ (homopolymer), 141526-68-3; Ni(p-pyr)TMHPP (homopolymer), 141526-73-0; Zn(p-NH$_2$)TMHPP (homopolymer), 141526-74-1; Ni(p-NH$_2$)TMHPP (homopolymer), 141526-76-3; Zn(p-NH$_2$)-TTPP (homopolymer), 133091-18-6; H$_2$(1,10-phen)(TMHPP)$_2$/H$_2$(p-pyr)TTPP (copolymer), 141526-69-4; Ni(p-pyr)TMHPP/Zn(p-NH$_2$)TMHPP (copolymer), 141526-77-4; AcNHC$_6$H$_4$-p-CHO, 122-85-0; H$_2$NNH$_2$, 302-01-2; CH$_3$OH, 67-56-1; O$_2$, 7782-44-7; H$_2$O, 7732-18-5; pyrrole, 109-97-7; 1,1-phenanthroline-4,7-dicarbonyl chloride, 130897-90-4; 2,5-diethoxytetrahydrofuran, 3320-90-9; *meso*-tri-p-tolyl(p-aminophenyl)porphyrin, 73170-32-8.

Photoresists on the Base of the Poly(hydroxyamines) and Poly(hydroxyamino esters)

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The linear poly(hydroxyamines) (PHA) and poly(hydroxyamino esters (PHAE) of various structures have been synthesized. PHA and PHAE exhibit peculiar photochemical and physicochemical properties which make them suitable for producing new high-sensitivity photoresists. The influence of chemical structure and molecular weight of the polymers on the photochemical characteristics and on the development kinetics of photoresists based on PHA and PHAE has been investigated.

Introduction

Linear poly(hydroxyamino ethers) (PHAE) synthesized by step growth addition reactions of secondary diamines or primary monoamines to bisphenol diglycidyl ethers [1-3] are under intensive investigation due to the opportunity of application in electrophotography.[4-6] In the presence of halogen-containing acceptors, for example, CBr$_4$, PHAE are oxidized under the action of light. The mechanism of photochemical transformation, in which a charge-transfer complex (CTC) plays the main role, was studied in detail in papers[7,8] The CTC is formed between the acceptor and an electron-donor amino group in polymer chain. The main product of photooxidation in such systems is a polycation with the structure dependent on the structure of the amine fragment. With the transition from nonpolar polymer to ionic polymeric photoproduct, the solubility changes resulting in selective dissolution between exposed and unexposed area making the films based on PHAE useful as photoresists.[9-11] It is important to note that the regarded systems possess some advantages in comparison with the known resists based on CBr$_4$[12-14] as the former ones have higher sensitivity due to the optical amplification. The optical amplification of the latent image is realized by the flood irradiation of the exposed sample with red and near IR light, $\lambda \geq 650$ nm. The light is absorbed only by the polycations (the latent image centers) that acts as an autosensitizer.

Many monoamines as well as diamines were used for the synthesis of PHAE described in the recent works.[1,2,15,16]

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Table I: Synthesis Conditions and Some Characteristics of PHA and PHA

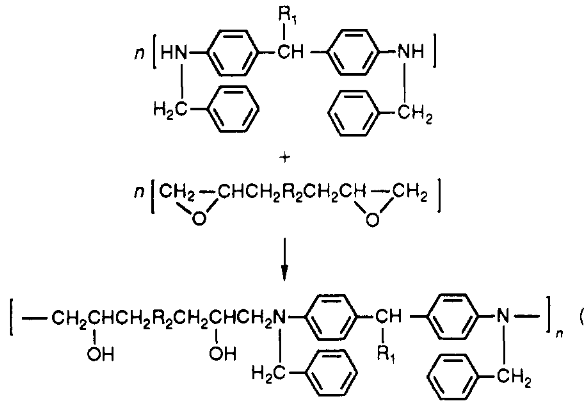
oligomer	synth conditions temp, °C	synth conditions time, h	M_n	n	T_g, °C beginning	T_g, °C end
I	110 ± 2	7.5	3100 ± 800	5.5 ± 1.5	58	63
II	110 ± 5	10.5	5430 ± 1070	8.6 ± 1.7	67	77
III	130 ± 2	115	5300 ± 900	7.6 ± 1.3	80	95
III	110 ± 2	115	3100 ± 400	4.5 ± 0.6	80	95
III	110 ± 5	17	1600 ± 200	2.3 ± 0.4	83	89
III	110 ± 5	17	1400 ± 200	1.9 ± 0.6	82	87
IV	160 ± 2	3.5	1200 ± 200	1.7 ± 0.2	55	58
V	160 ± 3	19	1900 ± 400	2.2 ± 0.4	77	87
VI	120 ± 2	133	1900 ± 500	1.9 ± 0.5	85	95

At the same time in these reports only the 2,2-bis(4-[(epoxypropyl)oxy]phenyl)propane was usually used as an electrophilic reagent. That limited the search of a PHAE structure with optimum physicochemical and photochemical properties.

In the present work the new poly(hydroxyamino ethers) and poly(hydroxyamino esters), marked also as PHAE, were synthesized. The structure of these PHAE changed not only at the amino fragment but at the ester or ether fragment as well. Furthermore the polyhydroxyamines (PHA) of various structures were synthesized. This article describes the results of an investigation of the influence of chemical structure and molecular weight of the polymers on the photochemical characteristics and kinetics of the development of the photoresists based on PHAE and PHA.

Experimental Section

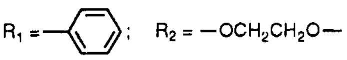
PHAE based on the *N,N'*-dibenzyl-4,4'-diaminodiphenylmethane or *N,N'*-dibenzyl-4,4'-diaminotriphenylmethane and the diglycidyl ethers of the bisphenols, ethylene glycol, or the diglycidyl esters of the cyclic dicarboxilic acids were synthesized using the known method



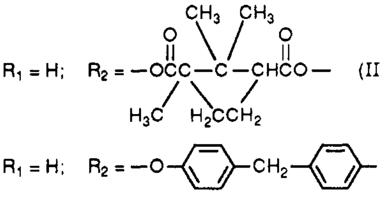
(1)

In the present paper we deal only with the polymers having the structures

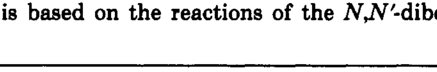
$R_1 = H$; $R_2 = —OCH_2CH_2O—$ (I)



(II)

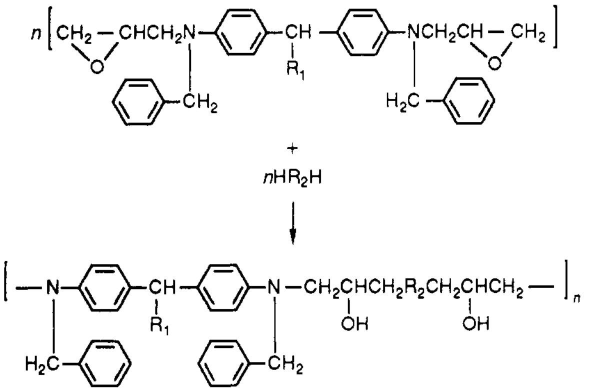


(III)



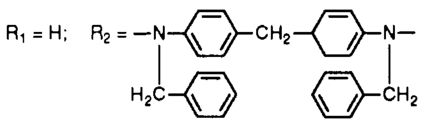
(IV)

A new method of synthesis of PHAE and PHA has been worked out. It is based on the reactions of the *N,N'*-dibenzyl-*N,N'*-bis(2,3-epoxypropyl)-4,4'-diaminodi- or triphenylmethane with dicarboxylic acids, primary monoamines, secondary diamines, ethylene glycol, and also bisphenols:

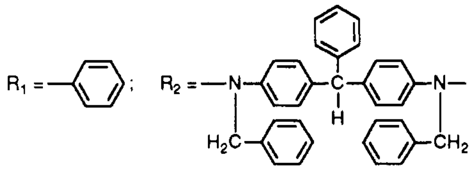


(2)

PHAE based on lower dicarboxylic acids and PHA as well were produced according to the reaction 2. The following polymers are discussed below:



(V)



(VI)

Reactions 1 and 2 were held in the melt of the equimolecular amounts of the reagents. A differential scanning calorimeter was used to determine the glass transition temperatures (T_g). The conditions of syntheses as well as the values of number-average molecular weight (M_n), the degree of polymerization (n), and T_g of PHA and PHAE are given in Table I. Molecular weights were measured using the vapor pressure osmometry method.

Samples were prepared by dissolving appropriate mixtures of the acceptor and PHAE or PHA in chloroform. CBr_4 was used as an acceptor. The mixtures were then solvent coated on polyethylene terephthalate substrata. All coatings were prepared under the inactive red light. The thickness of the molecularly doped polymer films was about 4–5 μm. In spite of the low values of M_n, all synthesized oligomers possess good film-forming properties.

Illumination from 150-W xenon lamp was passed through violet filter (spectral diapason 320–420 nm, incident power 6.5 × 10^{-4} W cm^{-2}). The visible and IR absorption spectra were recorded on Beckman DU-7 and Specord IR spectrophotometers, respectively.

The PHA and PHAE films can be used as negative and positive photoresists. In the first case the exposed films are developed by a mixture of $CHCl_3/CCl_4$ (1:1), in consequence of which the unilluminated part of the films is dissolved. In the second case the exposed films are developed by a mixture of $(CH_3)_2SO/CH_3OH$ (1:3) and the illuminated part of film is dissolved. The

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(16) Opfermann, J.; Horhold, H.-H.; Klee, J.; Wondraczek, R. *Acta Polym.* **1985**, *36*, 561.

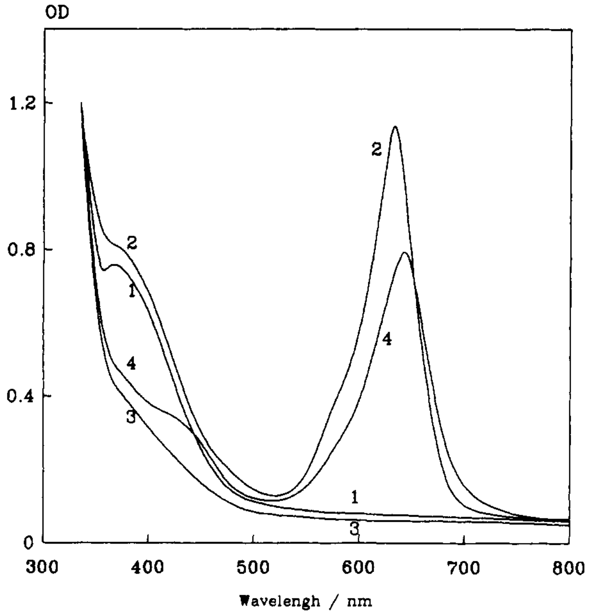
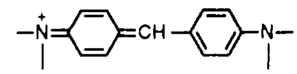


Figure 1. Optical absorption spectra of films I (1, 2) and II (3, 4) containing 50 wt % of CBr_4 before (1, 3) and after (2, 4) illumination. The illumination time was 16 (2) and 20 (4) minutes. OD is the optical density.

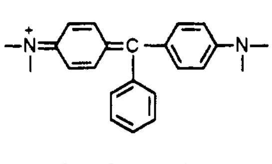
dissolution (development) occurred at room temperature. The mean development rate (R) has been determined as the reciprocal time of total dissolution of resist.

Results and Discussion

The exposure response curves that were obtained in the regime of direct coloration were analyzed to investigate the influence of the PHAE and PHA structure on the photooxidation efficiency. The colored photoproduct acts as an effective autosensitizer that permits the realization of optical amplification with an amplification coefficient >100 and to reach a sensitivity equal 0.1 mJ cm^{-2}. However the optical amplification process is not considered in this report. The structure of colored photoproduct is closely associated with the structure of amine fragment of PHA or PHAE. Oligomers which have a diaminodiphenylmethane fragment in their structure give a polycation like Michler's hydrol blue at the photo oxidation:[6,7,17]


(MHB)

Upon illumination of PHA or PHAE containing a diaminotriphenylmethane fragment in the presence of an acceptor, the malachite green fragment is formed:[7]


(MG)

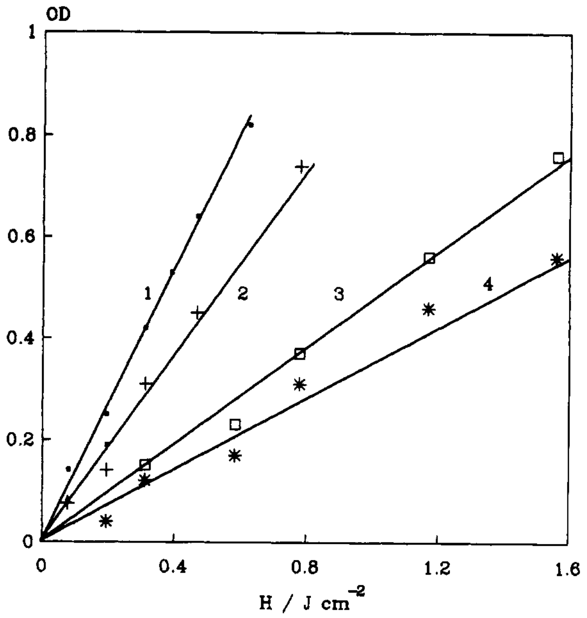


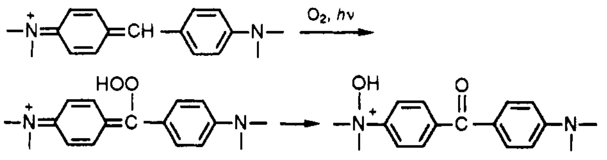
Figure 2. Plots of a colored product optical density at λ_{max} = 630 nm (1, 3) and λ_{max} = 640 nm (2, 4) as a function of the exposure for films I (1), II (2), V (3), and VI (4) containing 50 wt % of CBr_4.

Table II. Quantum Yield (φ) of the Polycation Formation

oligomer	M_n	φ	oligomer	M_n	φ
I	3100	0.030	III	1400	0.010
II	5430	0.006	V	1900	0.010
III	5300	0.025	VI	1900	0.001
III	1600	0.018			

Figure 1 shows the absorption spectrum of films I and II before and after illumination. The broad band over the range 330–480 nm belongs to the CTC.[7,8] It is seen in Figure 1 that the MHB has absorption band at λ_{max} = 630 nm and MG has two absorption bands at λ_{max} = 440 and 640 nm. Figure 1 also shows that the colored product formation is not accompanied by the essential change of absorption in spectral region of illuminating light.

MHB is not stable under the action of light, apparently due to the oxidative destruction that leads to the formation of a structure like the Michler's ketone:



(3)

This reaction causes the change of absorption spectrum in visible region. The intensity of absorption band of MHB (λ_{max} = 630 nm) decreases and simultaneously the absorption in the region 300–450 nm increases. The reaction occurs only under the action of light; in the darkness the shape of absorption spectrum is not changed for several years. The substitution of the phenyl substitute for the H atom of methine group excludes the possibility of reaction 3. Really, the illumination by visible light and/or UV irradiation of MG did not lead to the changes of absorption spectra.

Figure 2 illustrates the exposure dependences of the optical density (OD) for PHA and PHAE of various structures. The OD values are given for the maximum of the absorption bands of the appropriate polycations. At the transition from diaminodiphenylmethane (films I, V) to diaminotriphenylmethane fragments (films II, VI) the decrease of the sensitivity is observed that is associated with the decrease of the quantum yield (φ) of polycation formation (Table II) and partly with the decrease of light absorption in CTC band (Figure 1). It is obvious in Figure 2 and Table II that the decrease of light sensitivity and φ takes place for the PHAE (I, II) as well as for the PHA (V, VI). To calculate φ the extinction coefficient values

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(17) Horhold, H.-H.; Klee, J.; Opfermann, J. GDR Patent 232289, 1986.

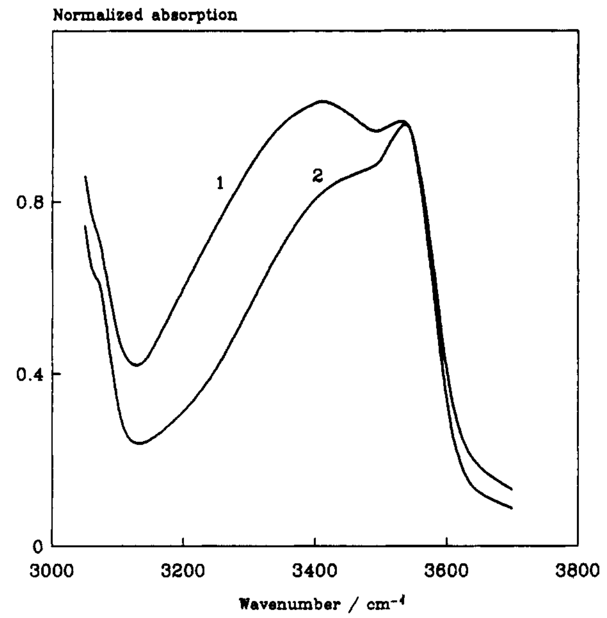

Figure 3. Infrared spectra of film IV at 24 (1) and 100 (2) °C. The film thickness was 12 ± 2 μm.

1.47×10^4 and 1.04×10^5 M^{-1} cm^{-1} for MHB and MG were used, respectively.[18]

The φ values are essentially smaller for PHA than for PHAE at the same M_n (Figure 2, Table II). Consideration of IR spectra of oligomer films has shown that the absorption band of the OH valence vibrations has the complex shape (Figure 3). The comparative analysis of position of components of the considered complex absorption band in the obtained IR spectra testifies that the high-frequency component (3535 cm^{-1}) belongs to the valence vibration of the spare OH group at the secondary C atoms of macrochain. But the low-frequency component one is caused by the presence of hydrogen bond complexes of —OH···N< type in PHA and in addition of —OH···O< type in PHAE. It is obvious, that the hydrogen bond between H atom of hydroxyl group and N blocks amine group and prevents the phototransfer of electron to acceptor following the photolysis reaction. The competition of ester or ether groups with amine groups in reaction of formation of hydrogen bond can provide the increase φ in PHAE in comparison with PHA. The additional proof of hydrogen bond formation is the shape change of IR absorption band of OH groups upon heating. The increase of temperature leads to a decrease in the intensity of the band component associated with H complexes, which testifies to its temperature dissociation.

We have found, that an increase of M_n of oligomers leads to a increase of the light sensitivity of layers based on PHA and PHAE (Figure 4). The displacement of the exposure response curves to the region of smaller expositions at the increase of M_n is accompanied by the increase of φ (Table II). An especially strong dependence of φ on M_n is observed at small M_n (1000–2000). This regularity can be explained if we assume that intramolecular transfer of positive charge between neighboring amine fragments of the macrochain can occur after the phototransfer of electron from the amine group to acceptor. Under these conditions considerable thermalisation distance between the radical cation and electron is realized and the reaction of back transfer of charge becomes hindered. It is obvious that the probability of the radical cation motion will be increased at the increase of the macrochain length and M_n.

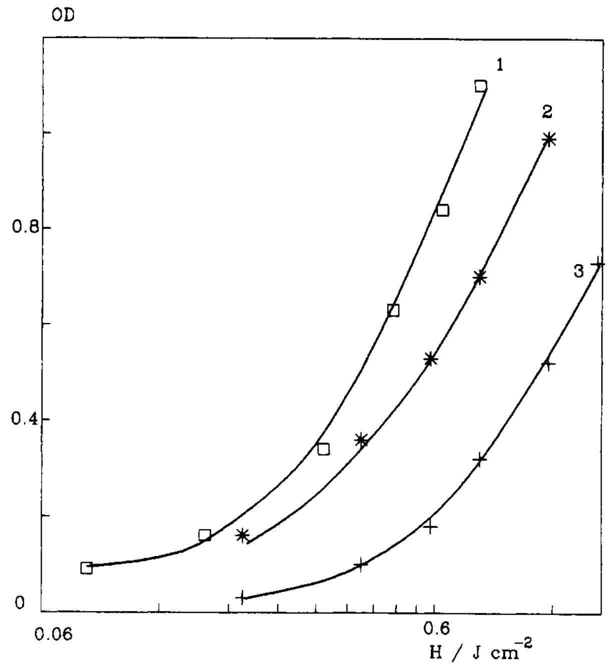

Figure 4. Exposure response curves for films III containing 50 wt % CBr_4 at M_n = 5300 (1), 1600 (2), and 1400 (3).

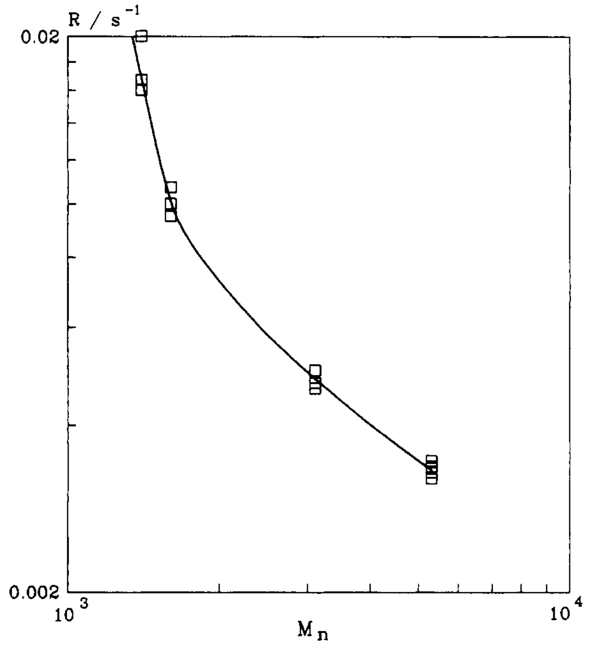

Figure 5. Effect of M_n on dissolution rate of unexposed films III containing 50 wt % CBr_4, 4.5-μm thickness.

At the change of M_n the kinetics of the dissolution (development) process changed essentially. The R of unilluminated films decreased with an increase in values of M_n in the region 1600–5300 according to the well-known equation[12]

$$R = kM_n^{-\alpha} \quad (4)$$

where $k = 16.5$ s^{-1} and $\alpha = 1.0$ are parameters depending on polymer and developer.

At low concentrations of photoproduct or at small optical density (OD) the R of illuminated films also decreased with the increase of M_n. At the same time at large OD (>0.8) R weakly depends on M_n (Figure 6). The transfer to the larger M_n at constant OD or at constant conversion degree leads to the decrease of the development selectivity

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(18) Gordon, P. F.; Gregory, P. *Organic Chemistry in Colour*; Springer-Verlag: Berlin, 1983.

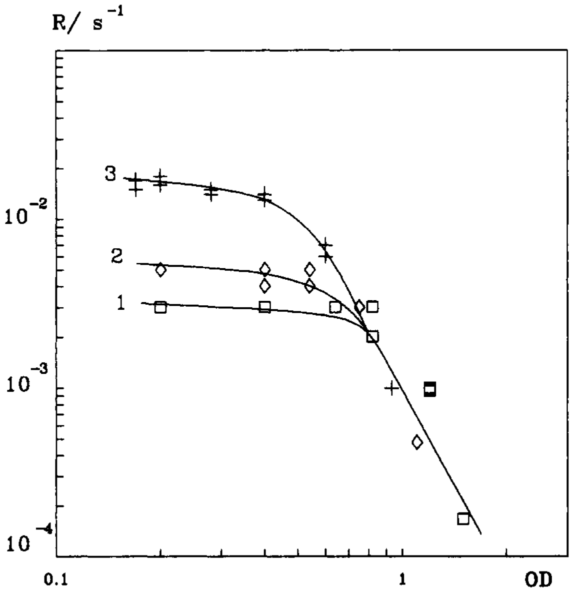

Figure 6. Dependences of dissolution rates on colored product optical density at λ_{max} = 630 nm for films III with M_n = 5300 (1), 3100 (2), and 1400 (3).

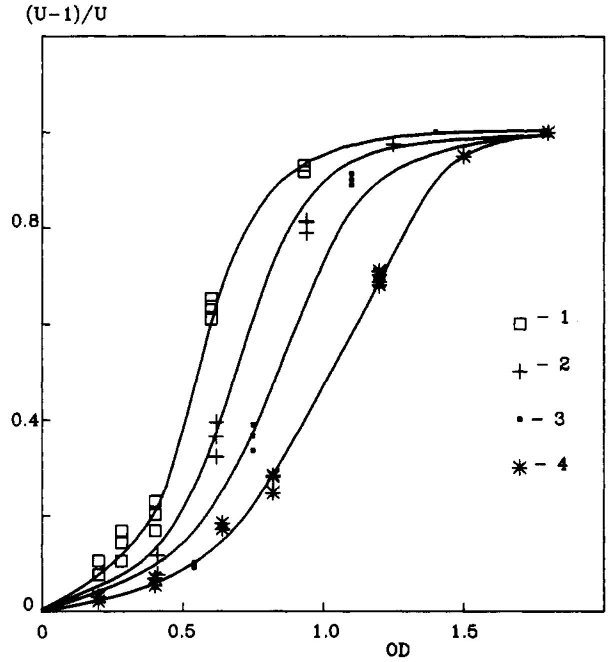

Figure 7. Dissolution characteristics vs the colored product optical density at λ_{max} = 630 nm for films III with M_n = 1400 (1), 1600 (2), 3100 (3), and 5300 (4).

(U; Figure 7). U is determined as the ratio of R of unilluminated film to R of illuminated one. It can be assumed that the values of parameters α and k in eq 4 decrease with an increase in the unsoluble polycation photoproduct concentration. Figure 8 illustrates the variation of U with OD at the maximum of the absorption band of photoproduct and shows that the structure of PHA or PHAE does not affect the development kinetics. To make it clear, the values $(U-1)/U$ are given on the ordinate axis in Figures 7 and 8. The experimental data in Figure 8 for oligomers with various structures but with equal M_n may be approximated by one curve. At the same time for constant OD U is decreased with an increase in M_n (Figure 8) independently on the structure.

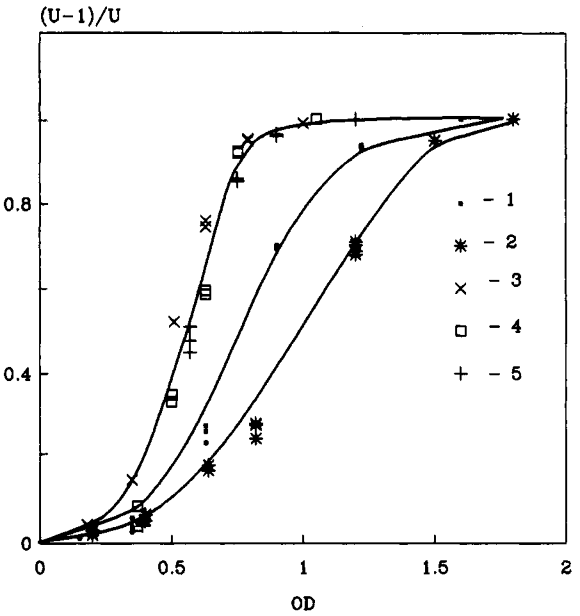

Figure 8. Dissolution characteristics vs the colored product optical density at λ_{max} = 630 nm for films I (1), III with M_n = 5300 (2), IV (3), and V (4), and at λ_{max} = 640 nm for film VI (5).

Conclusions

The comparative analysis of characteristics of photoresists based on PHA and PHAE of various structure enables us to determine the direction of the synthesis of optimal structures. It has been shown that PHAE possesses greater sensitivity than PHA. The use of PHAE with diaminodiphenylmethane fragments is more preferable than PHAE with diaminotriphenylmethane fragments. Apparently, PHAE with M_n < 5000–8000 must be used for the negative process due to the decrease of U at the increase of M_n.

Acknowledgment. We thank Dr. A. Grishina for many helpful discussions.

Registry No. I, 141377-35-7; II, 141377-37-9; III, 137661-51-9; IV, 141377-38-0; V, 141377-39-1; VI, 141377-41-5; *N,N′*-dibenzyl-*N,N′*-bis(2,3-epoxypropyl)-4,4′-diaminodimethane, 130036-13-4; triphenylmethane, 519-73-3.