

Differential Scanning Photocalorimetry Studies of 1,6-Hexanedioldiacrylate Photopolymerization Initiated by Some Organic Azides

M. J. M. Abadie,¹ O. O. Novikova,^{1,2} V. Yu. Voytekunas,¹ V. G. Syromyatnikov,²
A. Yu. Kolendo²

¹LEMP/MAO, Université Montpellier 2, S.T.L., Place Bataillon, 34095 Montpellier Cedex, France

²Kiev Taras Shevchenko University, Vladimirskaya Str. 64, Kiev 01033, Ukraine

Received 8 November 2002; accepted 1 February 2003

ABSTRACT: New types of radical photoinitiators, based on azido and diazido structures, were compared to the reactivity of pure xanthone by using a photocalorimetry technique. Our results show that these photoinitiators are

good candidates for radical polymerization. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1096–1101, 2003

Key words: azides; photopolymerization; photoinitiators; kinetics (polym.); reactive processing

INTRODUCTION

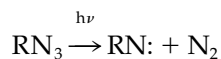
Radical photoinitiated reactions have been the focus of intensive investigation by both photochemists and polymer photochemists. This interest has increased because of the extensive scope of application of such reactions in creating new synthetic materials of technological importance. The popularity of this method is attributed to the ease of conducting the photoinduced radical reaction and the high selectivity and universality of these materials.

EXPERIMENTAL

Chemicals

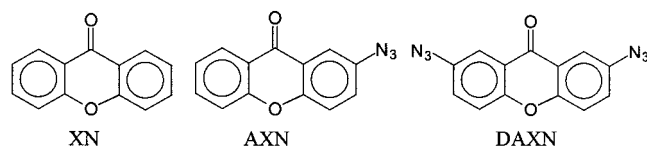
The ability of organic azides to decompose with formation of reactive species is well established.¹ Organic azides are widely used as photocuring agents in polymer composites for various purposes.^{2,3}

Decomposition of organic azides occurs according to the following scheme:



A nitrene biradical is, in most cases, the primary product of photolysis^{1,4} of azides. Light sensitivity to certain ranges of UV and visible light and the quantum

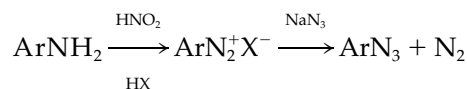
yield of azide photolysis are determined by their chemical structure and experimental conditions.⁵



The aim of the present work was to aid application of organic azides as new types of photoinitiators.

Azido derivatives of xanthone (XN), 2-azidoxanthone (AXN) and 2,7-diazidoxanthone (DAXN), were chosen as objects of investigation. The photoinitiating abilities of xanthone azides were previously studied with a dilatometry method and results were published.^{6,7}

Azides of xanthone were synthesized by aryl azides from their corresponding amines,⁸ using known methods of preparation:



Xanthone was nitrated by concentrated nitric acid⁹ and the product, a mixture of 2-nitro and 2,7-dinitro derivatives, was separated. The reduction of nitro compounds with SnCl₂ was carried out. Amino compounds were diazotated and then diazo compounds treated by aqueous solutions of sodium azides.⁶

The azides were repeatedly recrystallized from ethanol solution and their structure was validated by ¹H-NMR (DMSO, TMS) spectroscopy and elemental analysis. So in the NMR spectra of 2,7-diazidoxanthone: δ(H₁,H₈) -7.79 m.p., d.; δ(H₃,H₆) -7.62 m.p.,

Correspondence to: M. Abadie (abadie@univ-montp2.fr).

d.d.; $\delta(\text{H}_4, \text{H}_5) -7.78$ m.p., d.; in NMR spectra of 2-azidoxanthone (DMSO, TMS) -8.2 m.p., d.d.; $\delta(\text{H}_6) -7.92$ m.p., t.; $\delta(\text{H}_3) -7.46$ m.p., d.; $\delta(\text{H}_4) -7.6$ m.p., d.; $\delta(\text{H}_1, \text{H}_5, \text{H}_7) -7.6-7.85$ m.p., m.⁶

Xanthone azides are slightly colored crystal substances with good solubility both in polar and nonpolar solvents.

According to UV-spectroscopy data, absorption maxima of the azides are for 2-azidoxanthone: 260, 303, and 360 nm; for 2,7-diazidoxanthone: 270, 324, and 375 nm.¹⁰ The photochemical properties of xanthone azides were studied in ethanol solution and polymer films by UV- and IR-spectroscopy. They revealed themselves as light-sensitive compounds, and quantum yields of their photolysis under irradiation of monochromatic light ($\lambda = 365$ nm) of Hg high-pressure lamp are in the interval 0.2–0.5.

DPC measurements

For study of the potential application of the specified compounds the convenient method of differential scanning photocalorimetry (DPC), described in detail in earlier studies,^{11,12} was chosen.

The DPC method is based on differential scanning calorimetry (DSC), capable of delicate thermal analysis (measurement of heat flow as a function of time). Polymerization reactions of vinyl monomers are exothermic in nature, which makes it convenient to measure such reactions using thermal analysis.

The device uses a UV-light origin (Hg high-pressure lamp, 200 W), fitted for irradiation of samples that are heated to an assigned temperature.

A DuPont 930 (Boston, MA) DPC apparatus with differential calorimeter 912 was used for our investigations. The device allows one to carry out the heating of two samples simultaneously with an indium standard. Program selection, monitoring, and calculations used an IBM PC-2 computer connected to the device.

Experiments

We used 1,6-hexanedioldiacrylate (HDDA) as the monomer, which is not polymerized in such conditions without an initiator. Initiators were dissolved in the monomer in 1 wt % amounts. Samples of 1.5 ± 0.5 mg weight were set up in standard DuPont aluminum pans. For equal distribution of the solution layer under investigation, samples were covered with a thin film of poly(ethylene terephthalate). Pans were fitted in the thermostatic head of the device and samples were irradiated by a UV-lamp (3 mW/cm² intensity).

According to our selected program, samples were heated to the necessary temperature, kept isothermally for 1 min, and then subjected to 5-min irradiation in isothermal conditions. In accordance with a

previous study,¹¹ the polymerization reaction can be followed by the exothermal dependency of heat flow versus time.

Calculations

The enthalpy of polymerization [ΔH_{exp} (J/g)], induction time (time of 1% monomer conversion), time of attainment of maximum on the DPC curve [peak maximum (s)], and the monomer conversion in this maximum (reacted at peak) were obtained from the reaction exotherm.^{2,3}

Monomer conversion was calculated according to the equation

$$C = \Delta H_{\text{exp}} / \Delta H_t$$

where ΔH_{exp} is the experimental enthalpy at time t (J/g) and ΔH_{theor} is the theoretical enthalpy (J/g), which is expressed as

$$\Delta H_{\text{theor}} = (f\Delta H_f) / M$$

where f is the number of double bonds in the molecule (only for similar double bonds), ΔH_f is the enthalpy of the double bond opening (J/mol), and M is the molecular weight of the monomer. For HDDA, $f = 2$, $M = 226$ g/mol, $\Delta H_f = 19.2$ kcal/mol,¹¹ and $\Delta H_t = 710$ J/g. For kinetic calculations, the assumption was made that the reaction can be described by the following differential equation¹²:

$$d\alpha_{(t,T)} / dt = k_{(T)} f(\alpha)$$

where α is the fraction of the converted monomer; $k(T)$ is the rate constant, which depends on temperature T ; and $f(\alpha)$ is a function that describes the hypothetical model of the reaction mechanism.

When an autocatalytic kinetic model is used, the most common (according to Sestak and Berggren¹³) differential equation used is

$$R_{(T)} = d\alpha_{(t,T)} / dt = k_{(T)} \alpha^m (1 - \alpha)^n [-\ln(1 - \alpha)]^\delta$$

where α is the converted monomer and m , n , and δ are the partial reaction order for the steps of initiation, propagation, and termination, respectively. At the beginning of the reaction, $\delta = 0$ and this reduces the preceding expression to

$$R_{(T)} = d\alpha_{(t,T)} / dt = k_{(T)} \alpha^m (1 - \alpha)^n$$

Values of $k_{(T)}$ were calculated on the primary step of the reaction, in the interval between the opening of the diaphragm and attainment of a maximum on a DPC curve.

TABLE I
Parameters Obtained from DPC Study of HDDA Polymerization in the Presence
of Xanthone Azides and Irgacure® 1700

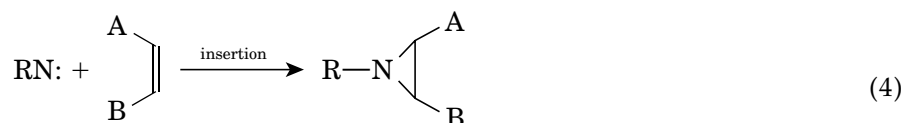
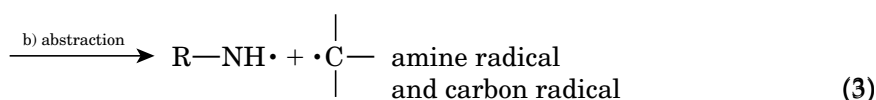
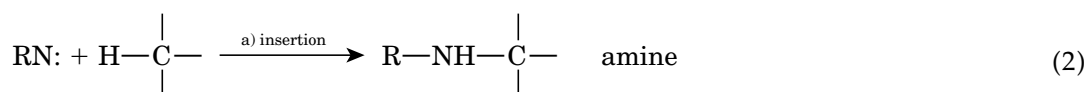
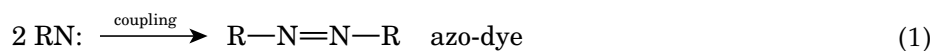
Compound	Temperature of experiment (°C)	Enthalpy (J/g)	Peak maximum (s)	Induction time (s)	Reacted at peak (%)	Rate constant <i>k</i> (1/min)	<i>E_a</i> * ^a (kJ/mol)
AXN	22.4	184.6	61.7	23.6	8.7	0.435	22.9 ± 1.3
	24.7	119.8	48.9	27.3	4.0	0.480	
	33.6	296.0	46.9	18.7	7.9	0.683	
	38.6	102.7	35.9	20.1	3.7	0.654	
	48.8	219.8	41.5	17.1	7.4	0.749	
	59.0	394.0	38.3	13.1	14.7	1.421	
DAXN	21.5	253.3	75.4	29.1	9.4	0.509	26.4 ± 0.4
	28.8	279.1	64.4	22.8	11.3	0.671	
	38.9	304.8	51.4	19.0	11.9	0.919	
	49.0	211.5	34.4	15.9	8.7	1.312	
	59.2	456.1	39.4	13.9	17.0	1.659	
	69.3	572.1	33.4	12.1	18.8	2.304	
IRG	79.5	565.1	32.8	11.3	26.2	3.069	10.1 ± 1.2
	23.9	420.0	4.6	2.8	15.7	21.993	
	33.8	489.2	3.4	1.7	15.2	22.857	
	43.8	522.4	3.4	1.7	17.0	26.447	
	53.9	584.3	3.7	1.6	21.9	31.837	
	64.1	570.0	3.6	1.7	15.7	34.307	

^a *E_a** activation energy, calculated according to Arrhenius equation.

Experiments were carried out under different temperatures and then the activation energy of the polymerization process was calculated according to the Arrhenius equation.

RESULTS AND DISCUSSION

The most typical reactions of nitrenes are the following¹:



Reaction (3) is the only one that causes the free-radical formation that is a necessary condition for initiating the polymerization process. Amino products are usually formed. This reaction occurs most readily in the presence of compounds with weak C—H bonds.¹

As previously shown,¹⁴ the formation of amino xanthone products is one of the main processes during the photolysis of azido xanthone derivatives. Azo-dyes and products of nitrene addition to the monomer double bond are not known. The products of carbonyl group reduction were also not detected. It can thus be suggested that, in the case of azido xanthone deriva-

tives, reaction (3) is crucial in the mechanism of polymerization initiation.

For estimation of initiation efficiency of investigated compounds as photoinitiators, the well-known radical initiator Irgacure® 1700 (IRG) was chosen, and experiments with IRG were conducted under similar conditions. It was observed that activation energy of the polymerization process in the presence of azides is higher than that for IRG (Table I). From data of Table I one can see that maximum conversion on the DPC curve, for polymerization in the presence of the azides under investigation, is similar to that for IRG, al-

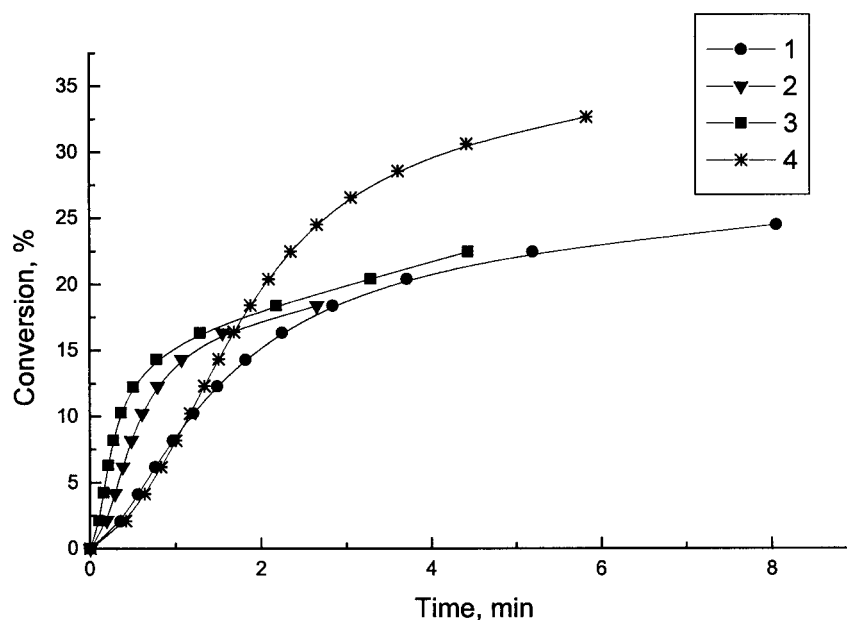


Figure 1 Dependency of HDDA conversion on time under 21.5°C in the presence of (1) DAXN, (2) DAXN and DEA (molar ratio 1 : 1), (3) DAXN and BDMA (molar ratio 1 : 1), (4) DAXN, BDMEA, and TEMPO (molar ratio 1 : 1 : 0.1).

though the rate constant of the process and enthalpy of reaction are higher for IRG, and the induction time and time to attain the maximum on the DPC curve is lower for IRG.

For investigation of the initiation mechanism, electron donors such as diethylamine (DEA) and benzyl-*N,N*-dimethylamine (BDMA) were added to the monomer solution, in a molar ratio of 1 : 1 with respect to azides. An increase in the rate of polymerization was observed in all cases (Figs. 1–3, Table II). This

phenomenon confirms the assumption that initiation by azides goes through the stage of hydrogen abstraction by nitrenes, leading to amine and carbon radicals. A decrease in the polymerization rate was observed after addition of 2,2,6,6-tetramethyl-piperidinyloxy free radical (TEMPO) to the reaction solution, which contains azide and DEA or DMA in ratios of 1 : 1 : 0.1 and 1 : 1 : 1, respectively. In the last case polymerization does not occur. When 0.1 molar TEMPO was added to a reaction solution that contains azide and

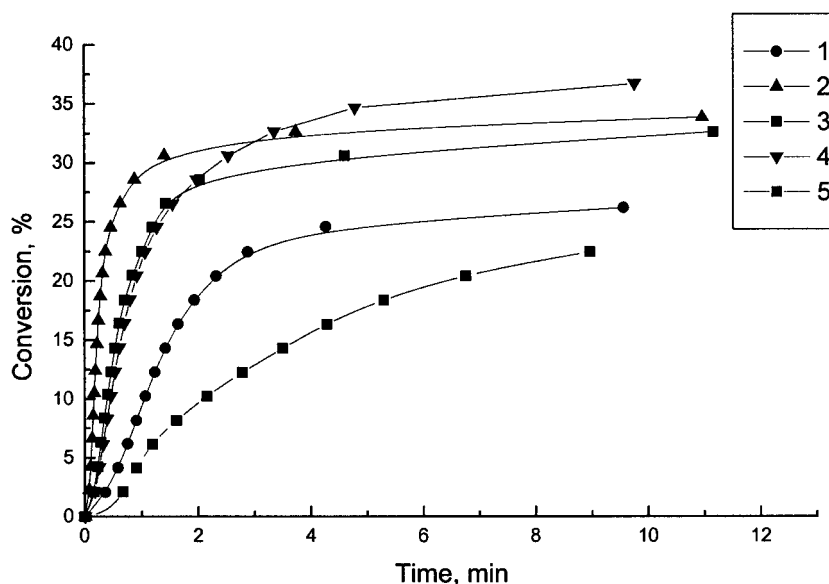


Figure 2 Dependency of HDDA conversion on time under 22.4°C in the presence of (1) AXN, (2) AXN and BDMA (molar ratio 1 : 1), (3) AXN, BDMA, and TEMPO (molar ratio 1 : 1 : 0.1), (4) AXN and DEA (molar ratio 1 : 1), (5) AXN, DEA, and TEMPO (molar ratio 1 : 1 : 0.1).

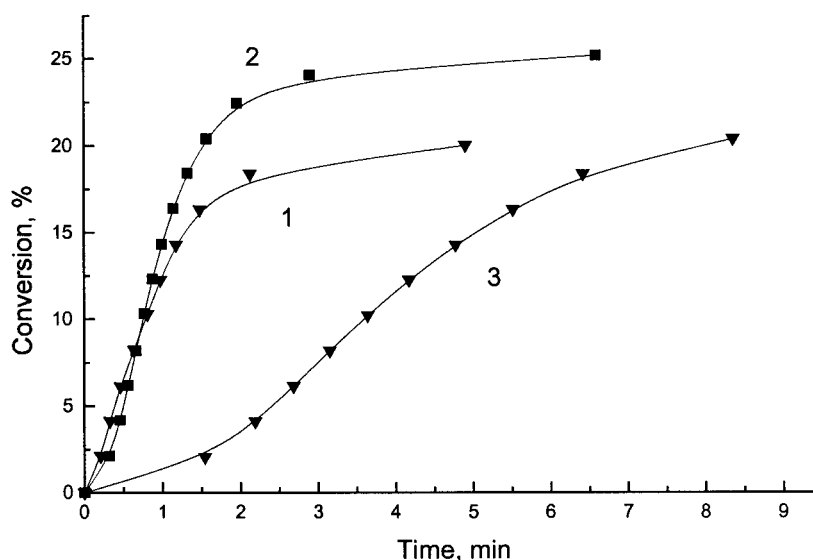


Figure 3 Dependency of HDDA conversion on time under 25°C in the presence of (1) XN and DEA (molar ratio 1 : 1), (2) XN and BDMA (molar ratio 1 : 1), (3) XN, BDMA, and TEMPO (molar ratio 1 : 1 : 0.1).

DEA or DMA in a 1 : 1 ratio, a decrease of rate was observed. In the case of DAXN, polymerization was not observed after the addition of even 0.1 molar TEMPO to the solution, which contains a 1 : 1 ratio of DAXN : DEA. Addition of TEMPO in the ratio of 1 : 1, or even 1 : 0.1, to the reaction solution with azides stopped the polymerization process. This confirms the radical character of initiation by azides and raises the possibility of estimating the amount of radicals taking part in initiation of polymerization. Less than 10% of the azide amount is involved in the initiation process. This is about one-third of the azide amount that photolysed (quantum yield of azide photodecomposition is 0.2–0.5, independent of photolysis conditions).

Polymerization of HDDA in the presence of xanthone does not occur at a noticeable rate. On DPC curves only a small peak was obtained. After the addition of DEA and BDMA in equimolar amounts to xanthone, an insignificant increase of the polymerization rate was observed (Fig. 3, Table II). It is known that, under UV-irradiation, photoreduction of the carbonyl group of xanthone occurs and a ketyl radical forms as an intermediate product.¹⁵ This process is also more effective in the presence of hydrogen donors.

Thus a change in the photolysis mechanism, with insertion of one or more azido groups in the molecule of xanthone, is observed. This fact can be explained by

TABLE II
Kinetic Parameters of HDDA Polymerization in the Presence of Xanthone, 2-Azidoxanthone, 2,7-Diazidoxanthone with Diethylamine, Benzyl-*N,N*-dimethylamine and TEMPO

Compound	Enthalpy (J/g)	Peak maximum (s)	Induction time (s)	Reacted at peak (%)	Rate constant (1/min)
XN, DEA (1 : 1)	177.5	63.7	37.7	8.1	0.951
XN, BDMA (1 : 1)	144.4	25.3	17.2	3.1	0.935
XN, BDMA, TEMPO (1 : 1 : 0.1)	150.5	326.1	217.2	7.1	0.209
AXN	184.6	61.7	23.6	8.7	0.435
AXN, DEA (1 : 1)	263.6	29.3	15.1	7.3	1.523
AXN, DEA, TEMPO (1 : 1 : 0.1)	158.1	89.7	70.1	3.3	0.636
AXN, BDMA (1 : 1)	240.3	14.1	8.3	8.6	4.381
AXN, BDMA, TEMPO (1 : 1 : 0.1)	232.0	24.9	16.3	5.4	2.546
DAXN	179.4	45.5	23.4	4.5	0.469
DAXN, DEA (1 : 1)	139.5	25.7	16.7	4.0	1.217
DAXN, BDMA (1 : 1)	170.3	14.7	10.2	3.7	2.215
DAXN, BDMA, TEMPO (1 : 1 : 0.1)	228.7	109.3	53.8	10.7	0.438

changes in electron-excited levels of molecules of azidoxanthenes compared with xanthone.¹⁴

Initiation of the polymerization process by xanthone azides undergoes the stage of hydrogen abstraction by nitrenes, thus generating amine and carbon radicals.

Investigation of 2-azidoxanthone and 2,7-diazidoxanthone confirmed that they are good photoinitiators of radical polymerization of vinyl monomers and their efficiency can be greatly increased by the addition of electron donors.

CONCLUSIONS

The azido derivatives of xanthone, 2-azidoxanthone and 2,7-diazidoxanthone, investigated in this study appear to be good photoinitiators for the radical polymerization of vinyl monomers and their efficiency can be greatly increased by the addition of hydrogen-donating compounds. This can be explained by the change of photolysis mechanism with the insertion of one or more of the azido groups in the xanthone molecule. Dissociation of the azido groups, instead of reduction of the carbonyl group, was observed.

Thus, initiation of the polymerization process by xanthone azides undergoes the stage of hydrogen abstraction by nitrenes, thus generating amine and carbon radicals.

References

1. Scriven, E. F. V. *Azides and Nitrenes: Reactivity and Utility*; Academic Press: New York, 1984.
2. Abadie, M. J. M. *Funct Mater (Ukraine)* 1998, 5, 296.
3. Cowie, J. M. G. *Polymers: Chemistry and Physics of Modern Materials*; Blackie Academic and Professional: Glasgow/London, 1996.
4. Lwowski, W., Ed. *Nitrenes*; Interscience: New York, 1970.
5. Novikova, O. O.; Avramenko, L. F.; Grigorenko, T. F.; Syromyatnikov, V. G.; Neduzhy, S. A.; Kolendo, A. Y.; Lysenko, N. S.; Ol'Hovic, L. A.; Prot, T.; Golec, K. *Funct Mater (Ukraine)* 1998, 5, 384.
6. Novikova, O. O.; Kolendo, A. Y.; Syromyatnikov, V. G.; Avramenko, L. F. *Ukr Khim Zh (Russ Ed)* 1997, 9, 65.
7. Novikova, O. O.; Kolendo, A.; Syromyatnikov, V. G.; Avramenko, L. F.; Prot, T.; Golec, K. *Polymeri* 2001, 46, 406.
8. Smith, P. A. S.; Hall, J. H. *J Am Chem Soc* 1962, 84, 480.
9. Kijosi, H. *J Chem Soc Jpn Ind Chem* 1968, 71, 463.
10. Novikova, O. O.; Avramenko, L. F.; Lysenko, N. S.; Syromyatnikov, V. G. *Ukr Khim Zh (Russ Ed)* 1998, 64, 123.
11. Pappas, P., Ed. *Radiation Curing*; Plenum Press: New York/London, 1992.
12. Abadie, M. J. M. *Eur Coat J* 1991, 11, 788.
13. Sestak, J.; Berggren, G. *Thermochim Acta* 1971, 31, 12.
14. Kolendo, A. Y.; Avramenko, L. F.; Grigorenko, T. F.; Novikova, O. O.; Ol'Hovic, L. A.; Kolisnichenko, T. N.; Mogilevich, R. V.; Serov, V. G.; Prot, T.; Golec, K. *Funct Mater* 2000, 7, 667.
15. Kachan, A. A.; Zamotaev, P. V. *Photochemical Modification of Polyolefins*; K. Naukova dumka: 1990.