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Polyhydroxyetheresters from resin acids

Summary — Six new polyetheresters were synthesized in polyaddition reaction in solution or in bulk. Polyaddition reactions have been carried out using the equimolar amounts of the adducts (RAAA), obtained in Diels-Alder reaction from resin acids (RA) and acrylic acids (AA), with three various epoxy resins with addition of adipic acid (AAd) or without it. The products obtained were characterized using FT-IR and ^{1}H NMR methods as well as on the basis of average molecular weight, nitrogen content and inherent viscosity measurements. The results of spectroscopic investigations confirmed RAAA adducts structures and epoxy ring opening in polyaddition reaction of epoxy resins with RAAA as well. Thermal stability of the products has been tested using TGA method. It was found they were rather stable at temperature up to 250—300 °C. The presence of AAd in the reaction mixture increases slightly thermo-oxidizing degradability but brightens the color and increases molecular weight of polyhydroxyetheresters. These products dissolve in majority of organic solvents because of the chemical structure (presence of OH groups and hydrophenantrene fragments).

Key words: resin acids, acrylic acid, adduct of Diels-Alder reaction, epoxy resins, polyhydroxyetheresters, thermal stability, solubility.

The last years, as a consequence of the oil crisis, the renewable raw materials (polysaccharides, triglyceride oils, proteins, oleoresin, natural rubber, etc.) became the alternative sources for chemical industry. Particularly, these natural materials have been used for the development of the environmentally friendly chemistry for synthesis of novel, polymer-based, materials. Oleoresin, the exudate of the coniferous trees, is principally constituted from resin acids (abietic acid, neoabietic acid, palustric acid, levopimaric acid etc.) and turpentine. Both the constituents can be used as raw materials in polymer synthesis. Resin acids, the main component, have a high chemical reactivity. They can react at the carboxylic group (by esterification, reduction, dehydrodecarboxylation, etc.) or at the double bonds (by Diels-Alder reactions with for example: maleic anhydride, acrylic acid, diallyl maleate, acrylamide, acrylonitrile). The obtained products were used in the formulations of adhesives, alkyd resins, paper sizing agents, varnishes, printing inks, odorants, and others [1—13].

Diels-Alder reactions' adducts of resin acids being, as a rule, di- or polyfunctional compounds, can be used as monomers in the polymer synthesis. There are many reports regarding the use of these adducts in the synthesis of: saturated and unsaturated polyesters [14, 15], polyamides [16—18], polyesterimides [19, 20], polyamidimides [21, 23], allylic resins [24, 25], polyimides [26], formaldehyde resins [2, 5, 6, 27], epoxy resins [4, 28—32] or polyhydroxyimides [33]. The presence of hydrophenanthrene moieties onto or in the polymer chain gives to these polymers valuable properties, such as: high solubility in common organic solvents, water repellence, high adhesion or reasonable thermal stability.

The aim of this work is to report the synthesis and characterization of some new polyhydroxyetheresters obtained by the reaction between three representative epoxy resins and the adduct of cycloaddition between resin acids and acrylic acid (see general Scheme A).

EXPERIMENTAL

Materials

The following epoxy resins were used: diglycidyl ether of bisphenol A (DGEBA) (SC Sintofarm SA, Romania) (epoxy equivalent weight = 345 g · eq^{-1}) was a commercial product; diglycidyl ether of hydroquinone (DGEHQ) (epoxy equivalent weight = 250 g · eq^{-1}) and diglycidylaniline (DGAN) (epoxy equivalent weight =

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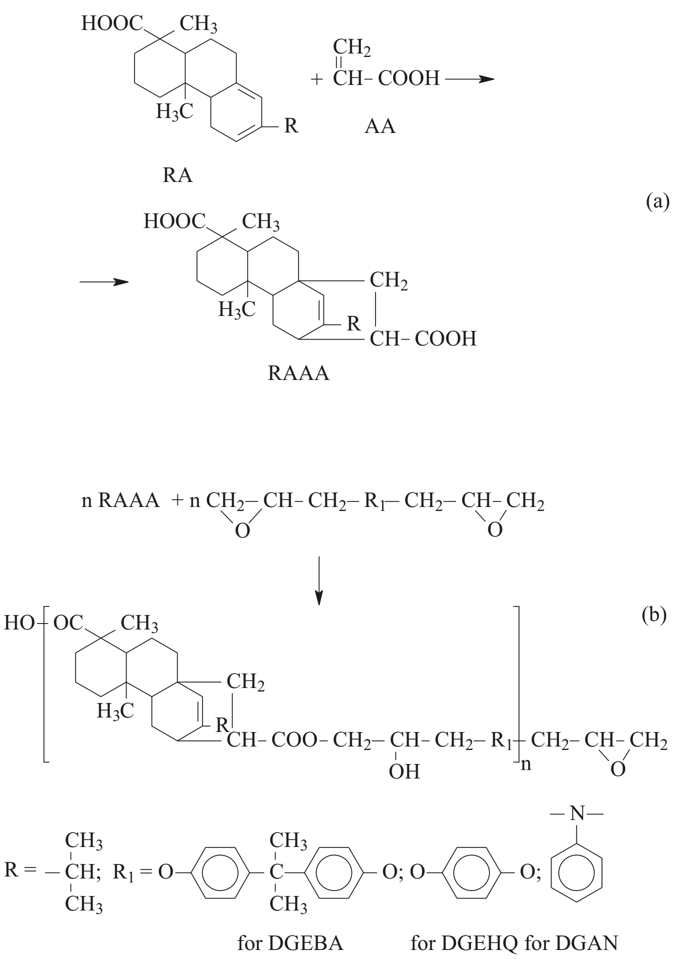

Scheme A. The synthesis of new polyhydroxyetheresters

175 g · eq^{-1}) were synthesized as described in ref. [33, 34].

Resin acids (RA) (acid number = 180 mg KOH · g^{-1}) were obtained from a commercial resin by twice recrystallization from acetone. Aniline (An), acrylic acid (AA), adipic acid (AAd), hydroquinone (HQ), sodium and potassium hydroxide and triethylbenzylammonium chloride (TEBAC) were analytical grade products.

The organic solvents were analytical grade products, or were distilled before use.

Synthesis of Diels-Alder reaction's adduct of resin acids with acrylic acid (RAAA) [Scheme A, reaction (a)]

A four-necked flask equipped with thermometer, mechanical stirrer, water condenser and N_2 inlet was charged with 100.67 g of RA, 26.4 g of AA, (1:1.1 molar ratio), and 0.27 g of HQ (1 wt. % referred to AA weight). The reaction mixture was heated, with stirring, at 140 °C for 2 h and at 170 °C for another 5 h. The crude reaction mass was cooled, powdered as fine grains and dissolved in ethyl ether at 25 g/dL concentration. The solution was washed to neutral pH with warm distilled water in order to remove the unreacted acrylic acid. Then, the solution was poured into a large amount of petroleum ether (boiling temperature = 28—60 °C) and a pale yellow precipitate was obtained. After filtration, the adduct of Diels-Alder reaction was dried overnight under vacuum at 70 °C. Finally, the product was recrystallized from acetone (yield 52 %, melting point = 221 °C).

Syntheses of polyhydroxyetheresters [Scheme A, reaction (b)]

A set of six polyhydroxyetheresters was obtained from the polyaddition reaction between RAAA, or RAAA/AAd mixture, and DGEBA, or DGEHQ, or DGAN, in the presence of TEBAC as catalyst, in solution or in bulk (Table 1). A representative experiment of the synthesis of the polymers in solution (sample 1, Table 1) has been done as follows. A four-necked reaction flask equipped with an oil bath, mechanical stirrer, N_2 inlet, condenser and thermometer was charged with 37.4 g (0.1 mol) of RAAA, 70 g of DGEBA (0.1 mol) and 26.8 g (25 wt. % referred to monomers weight) of solvent [*N*-methylpyrrolidone (NMP)/DMF, 1:1]. Then, the temperature was increased to 110 °C and maintained at this level for 15 minutes. After this, 0.4 g (1 wt. % referred to RAAA weight) of TEBAC was added. The reaction mixture was heated at 140 °C for 1 h and at 175 °C for several hours (according to the chemical structure of the epoxy resin, Table 1). Finally, the system was diluted with 50 mL of NMP/DMF = 1:1 mixture, cooled at room temperature and precipitated with a large amount of methyl alcohol. The resulted fibrous precipitate was washed with warm methyl alcohol and dried overnight under vacuum at 110 °C. After purification, nearly quantitative yield (89 %) was registered.

The bulk polymerization was performed at the same molar ratios and reaction conditions as the polymerization in solution. The obtained polymers were treated by pulverization and extraction with hot methanol. This time, the yields were somewhat higher in comparison with those registered for the polymerization in solution.

Methods of characterization

— Nitrogen content was determined in accordance with Kjeldahl method [35].

— The epoxy equivalent weights were determined using Sandner's method and were expressed as g · eq^{-1} [36].

— Molecular weight was determined by cryoscopic method using 1,4-dioxane as a solvent [37].

— Acid number was determined by direct titration with 0.1 N alcoholic KOH solution, in the presence of phenolphthalein as indicator.

— Viscosity measurements were performed with 0.5 g/dL solution in 1,4-dioxane at 25 °C, using an Ubbelohde viscometer with suspended level.

T a b l e 1. Reaction conditions of polyaddition between RAAA and epoxy resins and characteristics of the resulting polymers

Sample	Reagents (molar ratio)	Reaction time, h	Color	Yield, %	Amount of solvent, %	Number average molecular weight	Inherent viscosity dL/g	Nitrogen, %	T_g °C
1	RAAA/DGEBA (1:1)	10	pale brown	89	25	4050	0.22	—	78
		4	pale brown	96	—	5000	0.25	—	82
2	RAAA/DGEHQ (1:1)	10	pale brown	91	25	3790	0.19	—	70
		5	pale brown	98	—	3960	0.20	—	75
3	RAAA/DGAN (1:1)	10	pale red brown	88	25	3000	0.15	2.41	62
		5	pale red brown	92	—	3200	0.18	2.43	66
4	RAAA/AAd/ DGEBA (0.5:0.5:1)	10	pale brown	89	25	3920	0.23	—	71
		4	pale brown	94	—	4500	0.25	—	74
5	RAAA/AAd/ DGEHQ (0.5:0.5:1)	10	pale reddish brown	87	25	3430	0.21	—	64
		5	pale reddish brown	95	—	3890	0.24	—	67
6	RAAA/AAd/ DGAN (0.5:0.5:1)	10	pale red brown	89	25	3530	0.25	3.09	58
		5	pale red brown	95	—	3170	0.20	3.01	60

— Glass transition temperature (T_g) and melting points were registered by means of Mettler DSC 12E Toledo apparatus.

— FT-IR spectra were taken by Bio-Rad Digi Lab Division apparatus (Portmann Instruments) and using KBr pellets.

— ^{1}H NMR spectra were recorded using Avance DRX 400 (BRUKER, Rheinstatten, Germany) spectrometer. Samples were run at 50 °C, using tetramethylsilane as internal standard and acetone-d_6 and $CDCl_3$ as solvents.

— Thermogravimetric analysis (TGA) were carried out using MOM-Budapest of Paulik, Paulik-Erdey type derivatograph at the heating rate of 10 $^oC \cdot min^{-1}$, in air, in the temperature range from 25 to 600 °C.

RESULTS AND DISSCUSION

The structure of polymers

The chemical reactions involved in synthesis of RAAA and of the polymers are shown in Scheme A. As it was mentioned, RAAA was obtained from Diels-Alder reaction between RA and AA. In this reaction levopimaric acid (LA), one of the main components of resin acids, acts as diene and acrylic acid as dienaphile agent. The reactions start from a very low content of LA. As the diene addition advances, LA disappears and new LA is formed. Acids catalyse LA formation (abietic-type acids are converted to levopimaric form), so the reaction can go on. As a consequence, at the end of the reaction an important part of the resin acids was transformed into Diels-Alder reaction‘s adduct.

The structure of RAAA adduct was confirmed by FT-IR and ^{1}H NMR spectroscopy. Thus, in FT-IR spectrum of RAAA (Fig. 1a) the peak at 1700 cm^{-1} evidences the presence of COOH groups. The band characteristic for the double bond in the hydrophenanthrene moiety is observed at 1470 cm^{-1}. In ^{1}H NMR spectrum (Fig. 2a) the protons assigned to CH_3 or CH_2 groups resonate in the chemical shift range 0.92—2.15 ppm. The protons from the olefinic double bonds of the hydrophenanthrene moiety arise in the chemical shift range 5.5—5.6 ppm. The aromatic pattern in the chemical shift range 6.7—7.1 ppm represents the hydro phenanthrene nuclei. The car-

T a b l e 2. Solubility of polyhydroxyetheresters in various solvents[*)]

Sample (see Table 1)	*N*-methyl pyrrolidone	Dimethyl sulfoxide	DMF	1,4-Dioxane	Methyl ethyl ketone	Acetone	Cyclohexanol	Carbon tetrachloride	Benzene	Chloroform	Ethyl ether
1	++	++	++	++	++	++	+–	+–	+–	++	– –
2	++	++	++	++	++	++	++	+–	+–	++	– –
3	++	++	++	++	++	+–	++	+–	+–	++	– –
4	++	++	++	++	+–	++	+–	+–	+–	++	– –
5	++	++	++	++	++	++	++	+–	+–	++	– –
6	++	++	++	++	++	+–	++	+–	+–	++	– –

[*)] (++) Soluble at room temperature, (+–) soluble at heating, (– –) insoluble.

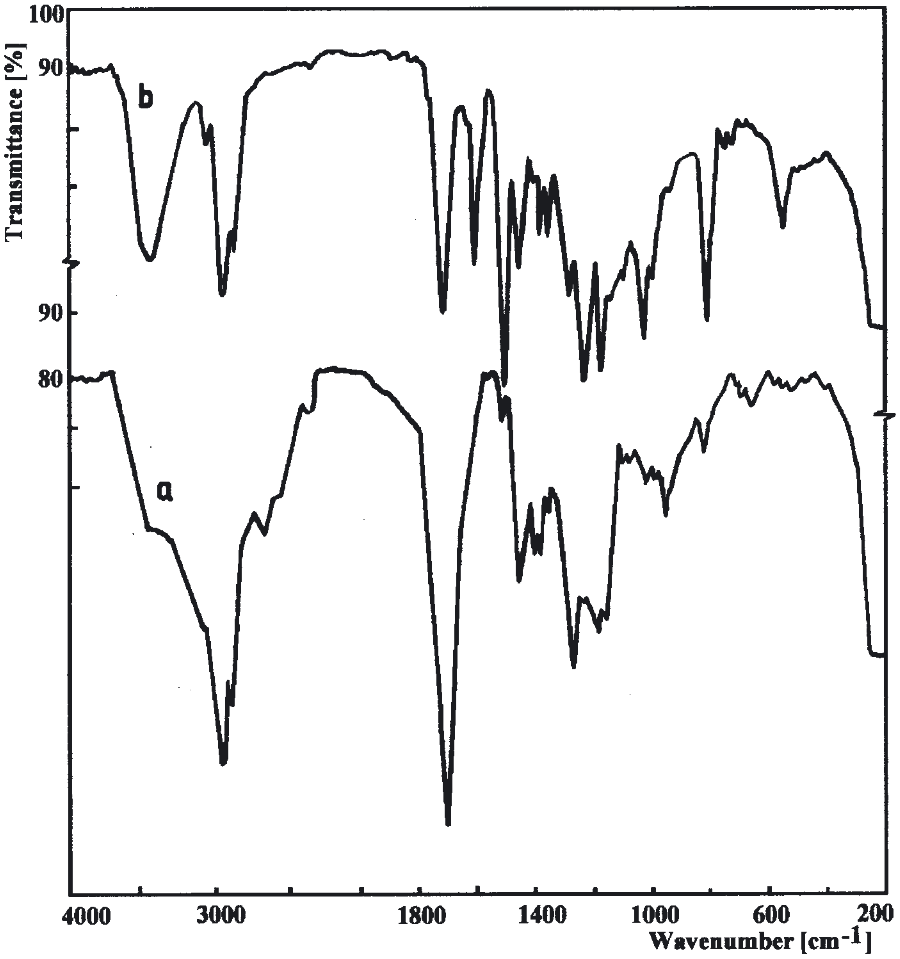

Fig. 1. FT-IR spectra of (a) RAAA and (b) polyhydroxyetherester obtained from RAAA/DGEBA

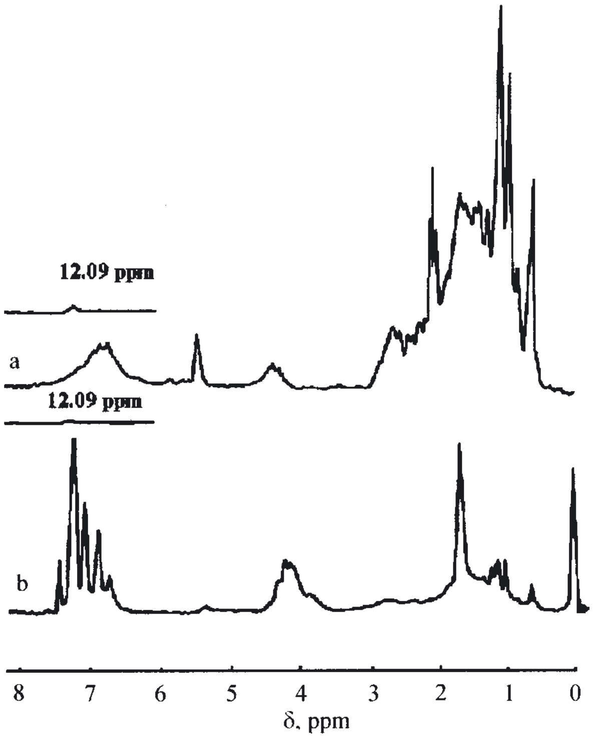

Fig. 2. ^{1}H NMR spectra of (a) RAAA and (b) polyhydroxyetherester obtained from RAAA/DGEBA

boxylic acid protons appear as a broad band with a chemical shift of about 12.09 ppm.

The polymerization reactions between RAAA, RAAA/AAd mixture and the three epoxy resins were conducted the way described in Experimental, in order to obtain linear polymers [32, 38]. These polymers are solid, low molecular weight materials, soluble in medium or high polar organic solvents (Table 2) and insoluble in ethyl ether, petroleum ether or aliphatic alcohols. The chemical structures of synthesized polymers, assigned in conformity with Scheme A, were identified by FT-IR, ^{1}H NMR and elemental analysis (nitrogen content, Table 1). In FT-IR spectrum (Fig. 1b) the strong absorption band observed at 3450 cm^{-1} represents OH groups resulted by the opening of the epoxy rings. The bands in the range 2880—2980 cm^{-1} represent CH_3 and CH_2 groups, from both hydrophenanthrene ring and glycerol moieties appeared as the results of the opening of epoxy rings. The bands specific to ester functionality are placed at 1720 cm^{-1} and at 1160—1240 cm^{-1}. The presence of a small peak at 915 cm^{-1}, characteristic for epoxy rings, confirms the existence of terminal epoxy groups and at the same time the reaction path at a molar ratio COOH/epoxy ring of 1:1. On the other hand, in ^{1}H NMR spectrum of the polymer (Fig. 2b) the bands in the range 0.8—2.1 ppm are due to CH_3 and CH_2 groups from the hydrophenanthrene moiety and DGEBA. The disappearance of the signal assigned to COOH groups situated at chemical shift of 12.09 ppm confirms their consumption in the reaction with epoxy groups. The opening of epoxy rings in the polymerization reaction is reflected both by the disappearance of the bands characteristic for them, placed in the range 2.5—3.5 ppm, and the appearance of the peak centered at the chemical shift of 4.15 ppm, due to the newly formed OH groups. The broadened peak centered at 5.4 ppm represents the olefinic double bonds from the hydrophenanthrene rings. The aromatic protons from epoxy moieties resonate, as the hydrophenanthrene nuclei, in the chemical shift range 6.62—7.25 ppm.

FT-IR and ^1H NMR spectra of polymers obtained from DGEHQ and DGAN did not differ too much from those obtained from DGEBA. Only the bands characteristic to monosubstituted benzene appear at the range 690—740 cm^{-1} for the polymers with DGAN. On the other hand in ^1H NMR spectrum in the range 7.85—8.15 ppm chemical shift the peaks specific to protons located in *orto* position to nitrogen substituent are presented.

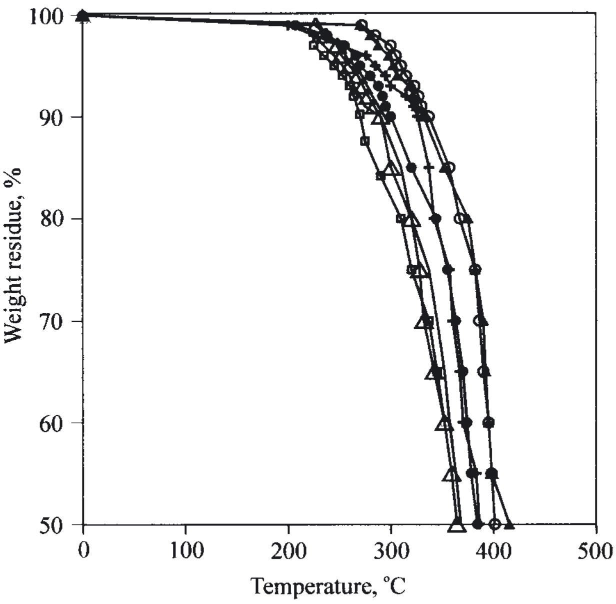

Fig. 3. TG curves of: RAAA/DGEBA (o); RAAA/DGEHQ (•); RAAA/DGAN (□); RAAA/AAd/DGEBA (▲); RAAA/AAd/DGEHQ (+); RAAA/AAd/DGAN (△)

Thermal stability of polyhydroxyetheresters

The thermal behaviour of the polymers obtained was estimated from their thermal degradation curves (Fig. 3). Thus, using the literature equations [39—42], the activation energy of degradation process, the order of the decomposition reaction and pre-exponential factor were calculated. For the same purpose some TG parameters as T_{10} (decomposition temperature at 10 % weight loss), T_{50} (decomposition temperature at 50 % weight loss) and W_{500} (weight loss at 500 °C) were also measured (Table 3). As it can be seen in Fig. 3 or in Table 3, the initial weight loss (T_{10}) was recorded at 330—335 °C for the polymers with DGEBA in composition (sample 1 and 4), at 300—325 °C for the polymers with DGEHQ (sample 2 and 5) and at 280—285 °C for the polymers with DGAN (sample 3 and 6). The decomposition process appears to be a two-stage type and is very fast between 330—400 °C for DGEBA polymers, between 310—400 °C for DGEHQ polymers and between 290—370 °C for DGAN polymers. Accepting T_{10}, T_{50}, W_{500} and activation energy of the degradation process as the criteria of the relative thermal stability, the data shown in Table 3 prove that the polyhydroxyetheresters synthesized with RAAA without AAd (Table 3, samples 1—3) exhibit high enough values for the above mentioned indexes (T_{50} between 370 °C and 400 °C, W_{500} of *ca.* 45 %, activation energies between 85 kJ/mol and 125 kJ/mol) and that they behave as fairly thermostable polymers. This finding can be explained by the existence of hydrophenanthrene moieties, known, *inter alia*, as thermostability promoters. From these the polymers based on DGAN (samples 3 and 6) show the worst stability.

When polyhydroxyetheresters obtained from RAAA have been compared with those synthesized with RAAA/AAd mixture (Table 3, samples 4—6) it has been found that the last ones present somewhat smaller values stability parameters. This is most evident in the case

Table 3. Thermal parameters of the polymers obtained in bulk polymerization[*)]

Sample (see Table 1)	T_{10}, °C	T_{50}, °C	W_{500}, %	Reaction order (*n*) evaluated by Swaminathan method	Kinetic parameter (ln A) evaluated by Swaminathan method min^{-1}	Decomposition activation energy, kJ/mol	
						evaluated by Swaminathan and Modhavan method	evaluated by Coats and Redfern method
1	337	401	45	1.12	18.34	109.66	123.44
2	300	384	46	1.06	19.05	111.84	112.12
3	280	368	44	0.89	11.67	76.70	83.23
4	332	415	45	1.33	15.77	97.26	110.12
5	326	386	46	0.77	12.37	75.67	65.23
6	280	354	46	1.16	15.65	87.39	77.06

[*)] Symbols — see text.

of the activation energies. The insertion of AAd moieties into the polymer structure probably more susceptible towards the thermooxidative degradation, caused a slight diminution of the positive effect exerted by RAAA. However, the presence of AAd in the polymer formula was justified by both the greater molecular weight and the paler color.

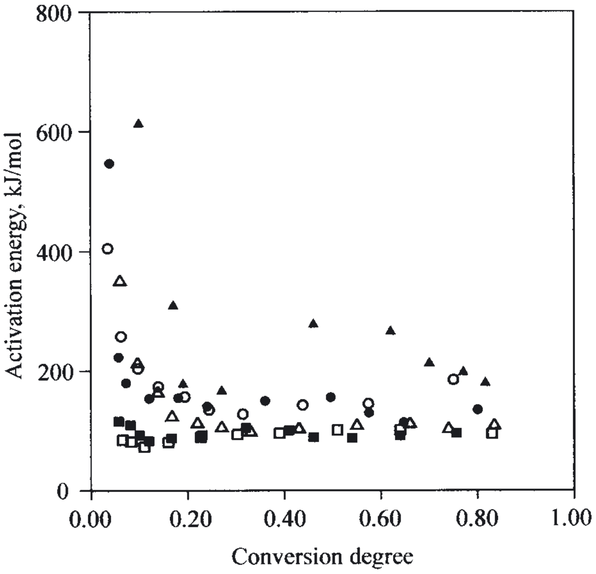

Fig. 4. Activation energy of degradation reaction versus conversion degree for: RAAA/DGEBA (o); RAAA/DGEHQ (•); RAAA/DGAN (△); RAAA/AAd/DGEBA (▲); RAAA/AAd/DGEHQ (□); RAAA/AAd/DGAN (▪)

As regards the activation energy of the degradation process (Fig. 4) one can observe that this strongly decreased in the initial stages, up to 0.1 conversion degree, and remain relatively constant in the range from 0.1 to 0.8 conversion degrees.

CONCLUSION

Six new polyhydroxyetheresters containing hydrophenanthrene moieties in their structures were synthesized and characterized. The polymers obtained show low molecular weights and are reasonably thermally stable solids, which can be used in the electrical engineering and electronic industry. Simultaneous presence of hydrophenanthrene moiety and of OH groups onto or in the polymeric chain gives them also high solubility in the majority of organic solvents.

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