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Polyhydroxyimides from resinic acids

Summary — Monomaleimide Diels—Alder adducts of levopimaric acid and diglycidyl ether of bisphenol A (DGEBA), and of levopimaric acid and diglycidyl ether of hydroquinone (DGEH), were prepared and then used to synthesize new polyhydroxyimides in the reaction (Scheme 2) catalyzed by benzyltriethylammonium chloride and carried out in a solvent (NMP) or without a solvent (Tables 1, 2). Chemical, thermal (TG, Table 3), and spectral (IR, ^1H NMR) methods were used to characterize the resulting products. The polymer products were found to be thermally stable and soluble in medium and high polarity solvents (Table 4). The solubility appears to have been imparted by pendant OH groups and phenanthrene rings present in the polymer chain.

Key words: resin acids, Diels—Alder adducts, polyhydroxyimides, IR and ^1H NMR spectra, thermal stability, solubility.

Rosin, a renewable raw material, consists mostly of resinic acids. The most important constituents are abietic acid and levopimaric acid. These acids are highly reactive and serve as a feedstock for synthesis of adhesives, printing inks, alkyd resins, paper sizing agents, odorants, polymers, *etc.*

Under mild reaction conditions, levopimaric acid forms Diels—Alder adducts with maleic anhydride, acrylonitrile, acrylic acid, fumaric acid, acrylate, *etc.* Under vigorous conditions, levopimaric acid is consumed, conjugated double-bond abietic types isomerize to yield the levopimaric form, and the abietic acid is transformed into Diels—Alder adducts [1]. Abietic acid and Diels—Alder adducts of levopimaric acid have been used in polymer synthesis to make formaldehyde resins, polyamides, polyamide-imides, polyesterimides, unsaturated polyesters, epoxy resins, allyl resins, *etc.* [2—12].

Introduction of phenanthrene nuclei into the polymer chain is expected to improve solubility, water resistance, and thermal stability.

The present paper reports on the synthesis and characterization of the epoxy resins modified by incorporation of Diels—Alder adducts of levopimaric acid with maleimide into the polymer chain to impart high thermal stability and to increase solubility.

EXPERIMENTAL

Materials

— Resin acids (*a. n.* = 180 mg KOH · g⁻¹) were separated from a commercial product as described in [13].

— Epoxy resin, diglycidyl ether of bisphenol A (DGEBA), was a commercial product (Sintofarm, Romania) with an epoxy equivalent of 345 g · eq⁻¹.

— Maleic anhydride, *p*-aminobenzoic acid, *p*-aminophenol, benzyltriethylammonium chloride, acetic anhydride, hydroquinone, sodium acetate, *p*-toluene sulfonic acid, and epichlorohydrin were analytical grade.

— Solvents were analytical grade, too, and were distilled just before use.

Measurements

The acid number (*a. n.*), was determined by titration with an alcoholic KOH solution in the presence of phenolphthalein until pink color appeared.

The epoxy equivalent weight was determined by the pyridinium chloride-pyridine methods as described in [14].

The number-average molecular weight was evalu-

ated in cyclohexane and DMSO by the cryoscopic method [15].

Melting points were measured on a Bötetius hot stage.

Viscosity measurements were taken at 20°C in a 0.5% (*w/v*) DMSO solution with an Ubbelohde viscometer.

IR spectra were recorded on a Specord M80 (Carl Zeiss) spectrophotometer (KBr pellets).

¹H NMR spectra were obtained with a JEOL-JNMC 60HL (Japan) instrument operated at 60 MHz and 50°C. Samples were run by using CDCl₃ and DMSO-d₆ as solvents and tetramethylsilane as internal standard.

Thermogravimetric analysis (TG) was carried out with a MOM-Budapest Paulik-Paulik-Erdey type derivatograph at a heating rate of 12°C/min.

Preparation of diglycidyl ether of hydroquinone (DGEH)

A mixture of 22 g (0.2 mol) hydroquinone and 185 g (2 mol) epichlorohydrin, 80 g isopropanol and 18 g water was heated on a water bath to 65°C in a four-necked round-bottomed flask equipped with a stirrer, thermo-

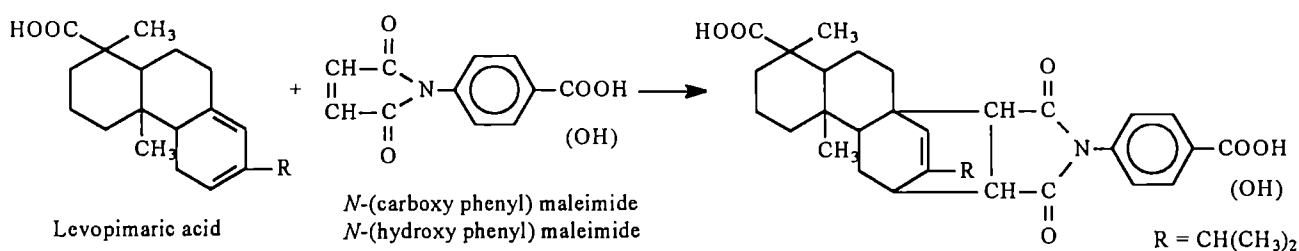
a dropping funnel. Then, maleic anhydride, 9.8 g (0.1 mol) dissolved in 60 mL acetone, was portionwise added at 15°C over a period of 1 h. The reaction mixture was stirred at room temperature for another 1.5 h. Finally, the amic acid precipitated as a pale yellow suspension. The suspension was filtered and the precipitate was washed with (30:70) acetone—acetic acid and dried in a vacuum oven at 150°C for 16 h (17.4 g; yield, 74%).

Into a four-necked flask, 17.4 g of the amic acid prepared, 50 mL acetic anhydride and 3 g fused sodium acetate were charged, stirred and heated at 80–90°C for 3 h. The reaction mixture was cooled and poured into a large excess of ice-water and stirred over 4 h. The resulting pale yellow precipitate was filtered, washed several times with distilled water, and dried under vacuum at 105°C for 16 h (12.4 g; yield, 73%; m. p., 224–227°C).

IR (KBr) 3450–3200 cm⁻¹ (carboxylic OH stretching), 1780 cm⁻¹, (imide I), 1730 cm⁻¹, (C=O imide), 1620 cm⁻¹ (C=C), 1400 cm⁻¹ (imide II), 1150 cm⁻¹ (imide III).

NMR (DMSO-d₆) 6.25 ppm (olefinic), 6.85, 7.45–7.86 ppm (aromatic) (Scheme 1).

Scheme 1



Diels-Alder adducts of levopimaric acid with *N*-maleimide

meter and a reflux condenser. The temperature was maintained for 4 h. Then, 80 g (0.4 mol) of 20% aqueous sodium hydroxide was added dropwise over a period of 1.5 h while maintaining the reaction temperature at 65°C and then stirred at that temperature for 3.5 h.

The reaction mixture was cooled and the aqueous phase separated. The organic phase was washed several times with distilled water to a neutral pH and distilled under vacuum at 135°C to remove the water and epichlorohydrin. Finally, 100 mL of toluene was added and a toluene-water heteroazeotrope and toluene were removed by vacuum distillation at the temperature of the reaction mixture 135°C.

The reaction mixture was purified by recrystallization from isopropanol. The reaction yield was 90%, the epoxy equivalent weight of the product was 160 g · eq⁻¹, and the number-average molecular weight was 310.

Synthesis of *N*-(*p*-carboxyphenyl)maleinimide (MPBA)

p-Amino benzoic acid, 13.7 g (0.1 mol), was dissolved in 100 mL acetic acid and charged into a four-necked flask fitted with a mechanical stirrer, thermometer and

Synthesis of (*p*-hydroxyphenyl)maleimide *p*-aminophenol (MPAP)

Into a four-necked flask equipped with a thermometer, mechanical stirrer and a dropping funnel charged with 10.9 g (0.1 mol) *p*-aminophenol dissolved in 150 mL of (1:2) acetone—acetic acid, 9.8 g (0.1 mol) maleic anhydride dissolved in 70 mL acetone was progressively added with stirring continued at 15°C for 1 h. The reaction mixture was maintained at 15°C with stirring continued for additional 2.5 h to yield a yellow orange precipitate (maleamic acid). The precipitate was filtered, washed with (1:2) acetone—acetic acid, and dried overnight under vacuum at 105°C (14.5 g; yield, 70%).

Maleamic acid, 14.5 g, was dissolved in 100 mL of (70:30) DMF—toluene, and charged into a reaction flask provided with a stirrer, a Dean Stark water trap and a reflux condenser, and a thermometer. The mixture was heated at 100°C, *p*-toluene sulfonic acid was added, and the temperature was increased up to a reflux temperature until the stoichiometric amount of water was recovered. Toluene was distilled off, the solution was allowed to cool and precipitated by pouring into an ice-water mixture with vigorous stirring. The filtered

product (dark orange) was washed with distilled water and dried overnight in vacuo at 105°C (13 g; yield, 90%). The product was recrystallized from isopropanol (m. p. 180–182°C).

IR (KBr) 3450–3300 cm⁻¹ (phenolic OH), 1778 cm⁻¹, 1720 cm⁻¹, 1140 cm⁻¹ (imide).

NMR (DMSO-d₆) 6.41 ppm (olefinic), 6.82, 6.91, 7.3–7.55 ppm (aromatic) (Scheme 1).

Synthesis of Diels–Alder adduct of levopimaric acid with monomaleimides

A 0.5-L reaction flask provided with a stirrer, N₂ inlet, thermometer and condenser was charged with 30.2 g (0.1 mol) resin acid, 18.9 g (0.1 mol) MPAP or 21.7 g (0.1 mol) MPBA, 1 g hydroquinone, bubbled with N₂ stream, was heated at 160°C for 1 h, at 170°C for 2 h, and at 200°C for another 2 h. The reaction mixture was cooled, dissolved in acetone under reflux, cooled and filtered. The precipitate was recrystallized from carbon tetrachloride to yield a white Diels–Alder adduct of levopimaric acid with MPBA (DAPBA) (36.92 g; yield, 71%; N, 2.82%). Recrystallization from acetone gave a pale brown product of Diels–Alder adduct of levopimaric acid with MPAP (DAAP) (32.1 g; yield 65%; N, 2.88%).

IR (KBr) 3500–3400 cm⁻¹ (carboxylic or phenolic OH), 2950–2870 cm⁻¹ (CH₂ in phenanthrene nuclei), 1700 cm⁻¹ (C=O), 1780 cm⁻¹, 1720 cm⁻¹, 1150 cm⁻¹ (imide).

NMR (DMSO-d₆), 0.9–2.1 ppm (CH, CH₂, CH₃ in phenanthrene nuclei), 5.64 ppm (olefinic), 6.82–7.21, 7.8, 8.4 ppm (aromatic), -5 ppm offset (COOH) (Scheme 1).

Synthesis of polyhydroxyimides

The Diels–Alder adduct of levopimaric acid with MPAP, 24.65 g (0.05 mol), or the Diels–Alder adduct of levopimaric acid with MPBA, 25.95 g (0.05 mol), and 30 g (0.05 mol) of DGEBA or 11.1 g (0.05 mol) of DGEH were charged in a 0.5-L four-necked flask equipped with a stirrer, thermometer, condenser and a heating mantle. The condenser was necessary when the reaction was carried out in the presence of a solvent (NMP). The reaction mixture was heated at 110°C and benzyltriethylammonium chloride was added (1% by weight). The temperature was raised to 180°C and maintained at that level for several hours (Tables 1 and 2). The reaction mixture was dissolved in NMP, cooled and poured into ice-water and kept overnight. The precipitate was filtered, washed with distilled water, and dried under vacuum at 105°C for 10 h. Polymers were obtained in quantitative yields (Scheme 2).

IR (KBr) 3500–3200 cm⁻¹ (carboxylic or phenolic OH), 2950–2870 cm⁻¹ (CH₂ in phenanthrene nuclei), 1700 cm⁻¹ (C=O), 1780 cm⁻¹, 1720 cm⁻¹, 1150 cm⁻¹ (imide), 1250–1200 cm⁻¹ (esteric).

NMR (DMSO-d₆), 0.9–2.18 ppm (CH, CH₂, CH₃ in

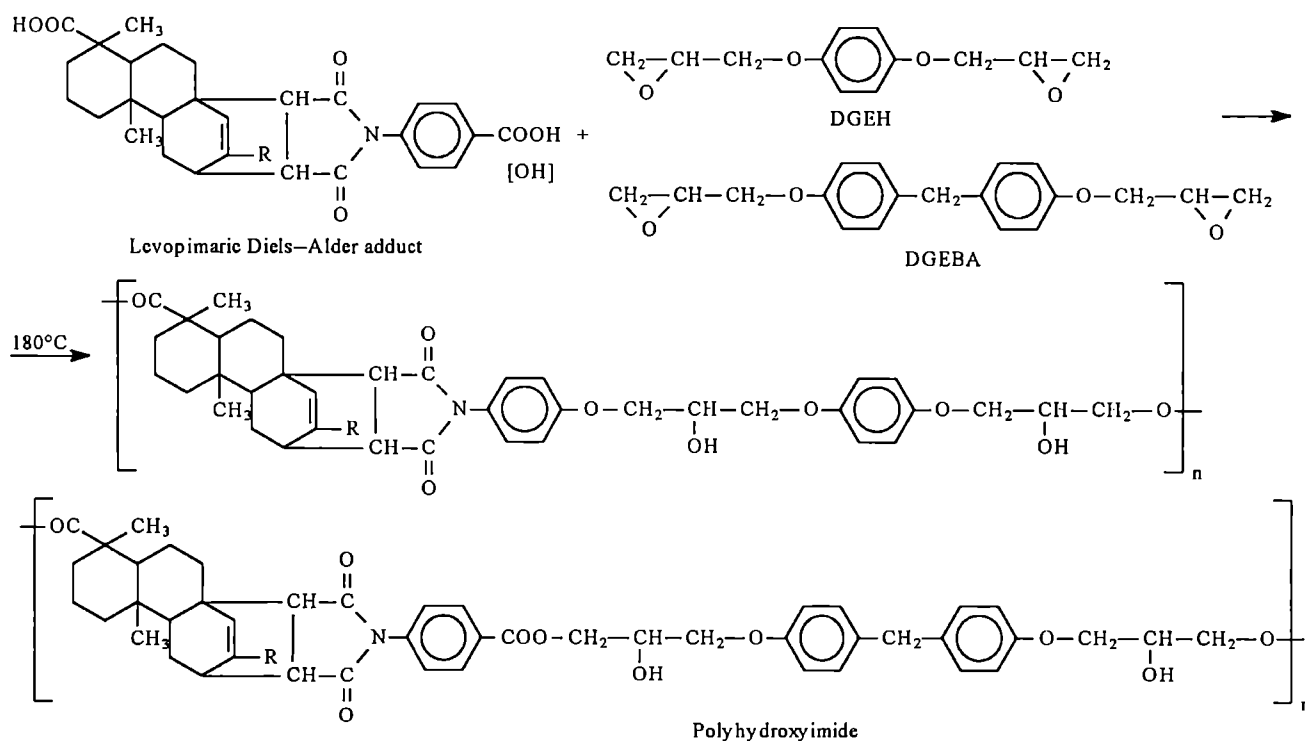
Table 1. The influence of temperature, time, solvent and catalyst on the step growth polymerization of monomaleimide Diels–Alder adduct of levopimaric acid with DGEBA

| Sample | Solvent | Reaction time, h | Reactant ratio (DGEBA/levopimaric adduct) | Reaction temperature, °C | Reaction yield, % | Levopimaric adduct | Catalyst | Inherent viscosity dL · g ⁻¹ |
|--------|---------|------------------|---|--------------------------|-------------------|--------------------|----------|---|
| 1 | NMP | 6 | 1/1 | 180 | 98 | HOOC-R-COOH | 1% | 0.1060 |
| 2 | NMP | 6 | 1/1 | 180 | 98 | HO-R-COOH | 1% | 0.0920 |
| 3 | NMP | 6 | 1/1 | 180 | 99 | HOOC-R-COOH | — | 0.0970 |
| 4 | NMP | 6 | 1/1 | 180 | 97 | HO-R-COOH | — | 0.0710 |
| 5 | — | 4 | 1/1 | 180 | 97 | HO-R-COOH | 1% | 0.0800 |
| 6 | — | 5 | 1/1 | 180 | 98 | HO-R-COOH | 1% | 0.0900 |
| 7 | — | 3 | 1/1 | 180 | 98 | HOCO-R-COOH | 1% | 0.0250 |
| 8 | — | 4 | 1/1 | 180 | 98 | HOCO-R-COOH | 1% | 0.0300 |
| 9 | — | 5 | 1/1 | 180 | 97 | HOOC-R-COOH | 1% | partially soluble |

Table 2. The influence of temperature, time, solvent and catalyst on the step growth polymerization of monomaleimide Diels–Alder adduct of levopimaric acid with DGEH

| Sample | Solvent | Reaction time, h | Reactant ratio (DGEBA/levopimaric adduct) | Reaction temperature, °C | Reaction yield, % | Levopimaric adduct | Catalyst | Inherent viscosity dL · g ⁻¹ |
|--------|---------|------------------|---|--------------------------|-------------------|--------------------|----------|---|
| 1 | NMP | 6 | 1/1 | 180 | 98 | HOOC-R-COOH | 1% | 0.0950 |
| 2 | NMP | 6 | 1/1 | 180 | 96 | HOOC-R-COOH | — | 0.0816 |
| 3 | NMP | 6 | 1/1 | 180 | 95 | HO-R-COOH | 1% | 0.0900 |
| 4 | NMP | 6 | 1/1 | 180 | 97 | HO-R-COOH | — | 0.0550 |
| 5 | — | 1 | 1/1 | 180 | 97 | HOOC-R-COOH | 1% | 0.1250 |
| 6 | — | 1.5 | 1/1 | 180 | 98 | HOOC-R-COOH | 1% | 0.2370 |
| 7 | — | 2 | 1/1 | 180 | 96 | HOCO-R-COOH | 1% | partially soluble |
| 8 | — | 2 | 1/1 | 180 | 95 | HO-R-COOH | 1% | 0.1160 |
| 9 | — | 4 | 1/1 | 180 | 91 | HO-R-COOH | 1% | 0.2160 |

Scheme 2



phenanthrene nuclei), 3.38, 3.87, 4.12 ppm (OH), 5.60 ppm (olefinic), 6.82–7.20, 7.92, 8.45 ppm (aromatic).

RESULTS AND DISCUSSION

Schemes 1 and 2 present the method applied to synthesize monomers and polymers. Monomaleamic acids were cyclodehydrated to yield the corresponding monomaleimide by using catalysts (fused sodium acetate of *p*-toluene sulfonic acid) or by distilling off a heteroazeotrope to remove water. Monomers were purified by recrystallization. They were characterized by IR and ^1H NMR spectroscopy. The IR absorption bands in the range 3400–3200 cm^{-1} are due to the carboxylic or phenolic OH. The presence of cyclic imide bonds was confirmed by the absorption bands at 1720 cm^{-1} (C=O), 1780 cm^{-1} and 1150 cm^{-1} . In the ^1H NMR spectra of monomaleimides, the specific peaks for these products are due to aromatic protons located at 7 ppm.

The Diels-Alder adducts of monomaleimides were prepared according to Scheme 1. The reaction mixture was purified by recrystallization from carbon tetrachloride or acetone. Melting points could not be determined, because the products containing phenanthrene rings in the molecules released CO_2 and H_2O at temperatures higher than 220°C [3, 16]. They were characterized by IR and ^1H NMR spectra and elemental analysis data (N, %). In the IR spectra, the peaks covering the range 2870–2950 cm^{-1} are specific to the phenanthrene ring.

In the ^1H NMR spectra of these Diels-Alder adducts, the major peaks cover the interval 0.9–2.1 ppm and are specific to the protons occurring in the phenanthrene ring. The weak band in a chemical shift range of 5.64 ppm appears to be due to olefinic protons [17]. The specific peaks for the aromatic ring correspond to the 7 ppm chemical shift.

The reactions between the Diels-Alder adducts and epoxy resins were catalyzed by benzyltriethylammonium chloride to provide exclusively linear polyhydroxyimide [18] at temperatures maintained at <200°C to avoid secondary reactions. The polymers were characterized by IR, ^1H NMR, TGA, and solubility. The IR spectra exhibited a strong absorption band in the range 3450–3200 cm^{-1} , specific to carboxylic or phenolic OH, and in the range 2950–2870 cm^{-1} specific to the phenanthrene ring. The presence of the cyclic imide linkages was confirmed by the absorption bands at 1780 and 1720 cm^{-1} . The absorption band at 1250–1200 cm^{-1} is specific to the polyester groups. Furthermore, the absence of peaks at 920–910 cm^{-1} (attributable to the epoxy terminal groups) confirms the formation of polyhydroxyimides.

In the ^1H NMR spectra of the polymers, the peaks covering the interval 0.9–2.1 ppm confirm the presence of protons of the phenanthrene ring. The peaks characteristics for the epoxy groups at 2.8 ppm disappeared and the peaks produced at 3.8–4.2 ppm confirm the formation of polyhydroxyimides. Disappearance of the peak corresponding to -COOH (-5 ppm) indicated the reaction path and appearance of polymers.

Thermal properties of polymers

Thermal properties of the polyhydroxyimides were evaluated by TG measurements (Fig. 1). The thermal behavior of the polymers is characterized by the para-

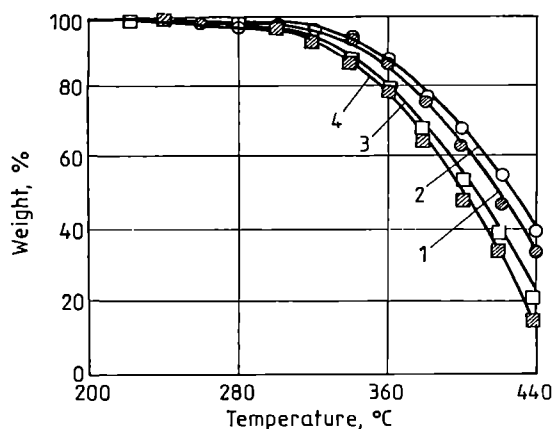


Fig. 1. Thermogravimetric curves: 1 — sample 6, Table 1; 2 — sample 9, Table 1; 3 — sample 6, Table 2, 4 — sample 8, Table 2

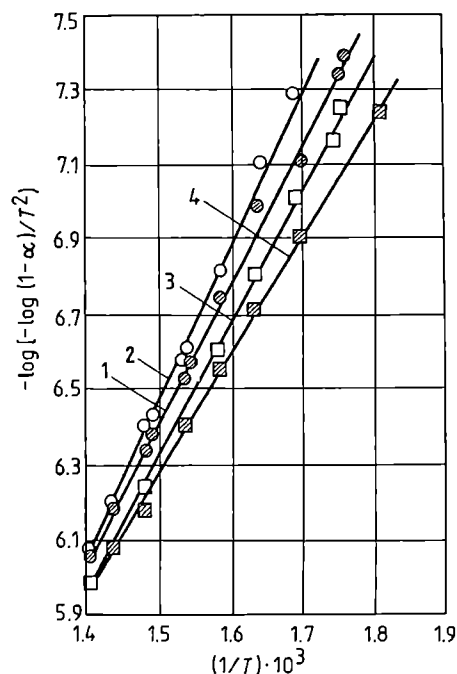


Fig. 2. Plots of $-\log[-\log(1 - \alpha)/T^2]$ vs. reciprocal decomposition temperature: 1 — sample 6, Table 1, 2 — sample 9, Table 1, 3 — sample 6, Table 2, 4 — sample 9, Table 2

Table 3. Thermal characteristics of some polyhydroxyimides

| Sample | Weight loss at given temperatures, °C | | | Activation energy for the decomposition reaction, $\text{kJ} \cdot \text{mol}^{-1}$ |
|-------------|---------------------------------------|-----|-----|---|
| | 10% | 20% | 50% | |
| 6 (Table 1) | 335 | 372 | 415 | 69.38 |
| 8 (Table 1) | 350 | 378 | 420 | 78.31 |
| 6 (Table 2) | 330 | 358 | 400 | 63.60 |
| 9 (Table 2) | 332 | 360 | 410 | 69.33 |

Table 4. Solubility of the polyhydroxyimides

| Sample | DMF | DMSO | NMP | Acetone | Benzene | Carbon tetrachloride |
|-------------|-----|------|-----|---------|---------|----------------------|
| 6 (Table 1) | ++ | ++ | ++ | +- | - | - |
| 8 (Table 1) | ++ | ++ | ++ | ++ | +- | - |
| 6 (Table 2) | ++ | ++ | ++ | ++ | +- | +- |
| 9 (Table 2) | ++ | ++ | ++ | ++ | ++ | - |

++ Soluble at room temperature, + soluble on heating, - insoluble, +- partially soluble or swelling.

eters listed in Table 3. The relative thermal stability of the polymers was estimated by comparing the energies of decomposition evaluated by the Coats-Redfern method [19] for the order of reaction $n = 1$. From Fig. 2, we calculated the activation energy of decomposition (Table 3). The polymers with the Diels-Alder adducts of carboxyphenylmaleimide on the chain showed the activation energies of decomposition high as compared with those of the polymers which contained the Diels-Alder adduct of hydroxyphenylmaleimide.

Solubility of polymers

The polymers synthesized were found to be soluble in medium and highly polar solvents (Table 4). This solubility is explicable in terms of the presence of pendant OH groups and the presence of the phenanthrene ring on the polymer chains, which reduces packing.

CONCLUSION

The reaction of Diels-Alder adducts of levopimaric acid with monomaleimide of *p*-aminophenol and *p*-aminobenzoic acid has been applied to prepare thermostable polyhydroxyimides. The Diels-Alder adducts of levopimaric acid with monomaleimide of *p*-aminobenzoic acid are more reactive with epoxy resins than are the Diels-Alder adducts of levopimaric acid with monomaleimide of *p*-aminophenol under the condition specified in Table 1. This is confirmed by an increase in the viscosity of polymers. The polymers with a high viscosity show a reasonable thermal stability: a 10% weight loss was observed between 335 and 350°C.

Both the pendant OH groups present on the polymer

chain and the phenanthrene nuclei in the polymer chain impart solubility in medium polar solvents.

REFERENCES

1. Stonecipher W. D., Turner R. W. in: "Encyclopedia of Polymer Science and Technology", Vol. 12., Interscience Publisher, John Wiley, New York 1970, p. 139.
2. Bicu I., Mustată F.: *Angew. Macromol. Chem.* 1993, **213**, 169.
3. Bicu I., Mustată F.: *Angew. Macromol. Chem.* 1994, **222**, 165.
4. Bicu I., Mustată F.: *Angew. Macromol. Chem.* 1996, **234**, 91.
5. Bicu I., Mustată F.: *Angew. Macromol. Chem.* 1997, **246**, 11.
6. Hoa L. T. N., Pascault J. P., My L. T., Son C. P. N.: *Eur. Polym. J.* 1993, **29**, nr 4, 491.
7. Maiti M., Adhikari B., Maiti S.: *J. Polym. Mater.* 1988, **5**, 201.
8. Ray S. S., Kundu A. K., Maiti S.: *Eur. Polym. J.* 1990, **26**, nr 4, 471.
9. Penczek P., Kicko-Walczak E., Smolovik E.: *Plast. Massy* 1977, **6**, 11.
10. Matynia T.: *Polimery* 1975, **20**, 7.
11. *Pol. pat.* 78 413 (1975).
12. *Pol. pat.* 65 215 (1972).
13. Desalbres L., Dubearnes R.: "Bull. Soc. Chem. France", 1958, 229, conf. CA., 52 Abst. 9627 (1958).
14. Cascaval C. N., Mustată F., Rosu D.: *Angew. Macromol. Chem.* 1993, **209**, 157.
15. Bonar R. U., Dimbat M., Stross M.: "Number-Average Molecular Weights", Interscience, New York 1958, Chap. 3.
16. Bicu I., Mustată F.: *Angew. Macromol. Chem.* 1998, **255**, 45.
17. Simons W. W., Zanger M.: "The Stadler Guide the NMR Spectra of Polymers", Stadler Research Laboratories, Inc., Philadelphia, Pa. 1973, p. 242.
18. Lunsford D., Banthia A. K., McGrath J. E.: *Polymer Preprints* 1981, **22**, nr 1, 194.
19. Coats W. W., Redfern J. P.: *Nature* 1964, **68**, 201.

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Od Redakcji

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