

Ketone Derivatives of Diels-Alder Adducts of Levopimaric Acid with Acrylic Acid and Maleic Anhydride: Synthesis, Characterization, and Polymerization

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ABSTRACT: Two new ketone-type derivatives were synthesized by the dehydrodecarboxylation of levopimaric acid acrylic acid adduct and of levopimaric acid maleic anhydride adduct in the presence of sulfonic catalysts. The two compounds were also synthesized by coupling of acrylic acid or maleic anhydride with dipimaryl ketone. These ketones, or rather ketone-diacids, were condensed with polyalkylenepolyamines to give poly(amide)s or poly(imide)s with good thermal properties. New crosslinked polymers

were obtained when these poly(amide)s or poly(imide)s were substituted with epichlorohydrin. The structures of the resulted ketone-diacids and polymers were investigated by the usual physical and chemical methods. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2240–2252, 2004

Key words: polycondensation; polyamides; polyimides; crosslinking; thermosets

INTRODUCTION

In the past resin acids, particularly abietic acid, have been extensively used as raw materials for new polymers with specific chemical structures and valuable properties. Owing to their three-cyclic structure, resin acids ought to present high enough chemical and thermal stabilities. But the unsaturated groups from the hydrophenthrene moiety make them vulnerable and give them characteristic chemical reactivity.¹

Before their use in polymer synthesis, resin acids were transformed, either into unsaturated monomers (acrylic, vinylic) or into bi- or polyfunctional compounds. For this purpose some routes, such as those shown below, were used:

- chemical transformation, via cycloaddition reactions, into diacids, dialdehydes, polybasic acids,^{1–6} or unsaturated compounds;⁷
- chemical modification by dimerization, disproportionation, or polymerization;^{3,8,9}
- the obtainment of epoxy derivatives;^{10–13}
- the obtainment of vinyl ester of abietic acid by transesterification in the presence of vinyl acetate^{14,15} and of allyl ester by esterification of sodium abietate with allyl halides;¹⁶
- the obtainment of abietic anhydride.^{17,18}

Recently, we described a new method for synthesis of such bifunctional compounds, consisting of the dehydrodecarboxylation of levopimaric acid in the presence of sulfonic-type catalysts.¹⁹ The reaction ended in a bisdiene, dipimaryl ketone (DPK). This was polymerized with 4,4'-diphenylmethanedimaleimide by a proper Diels-Alder polymerization.²⁰

The purpose of this article is to present the synthesis, characterization, and polymerization of ketones obtained by the dehydrodecarboxylation of acrylic acid levopimaric acid Diels-Alder adduct (APA) and of maleic anhydride levopimaric acid Diels-Alder adduct (MPA). The acronyms used in the present article for these two ketones are DAPK and DMPK, respectively. Having in their structure two acid groups, or two anhydride groups, these ketones have been polymerized by condensation with triethylenetetramine (TETA), the same polyalkylene polyamine which was used when APA and MPA were polymerized, too.²¹ This allowed us to perform a comparative study emphasizing the influence exerted by the carbonyl groups from the structure of the new poly(amide)s or poly(imide)s on their properties.

EXPERIMENTAL

Materials

Abietic acid, in its isomer form of levopimaric acid (PA), (acid number (AN) = 184 mg of KOH/g, 99%), APA (AN = 295 mg of KOH/g, 98.5%), and MPA (AN = 416 mg of KOH/g, 99%) were prepared and purified as described in ref. 21. DPK (AN = 1.0 mg of

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KOH/g, >98%) was prepared and purified as described in ref. 19. TETA (Fluka AG, Buchs, Switzerland, 97%), acrylic acid (AA; Fluka, > 98%), epichlorohydrin (EC; Fluka, >98%), toluene-4-sulfonic acid monohydrate (TSA; Aldrich, Steinheim, Germany, 98%), and maleic anhydride (MA; Aldrich, 99%) were used as received. The organic solvents used were analytical grade.

Measurements

AN was determined with 0.1 N aqueous KOH in the presence of phenolphthalein with acetone as solvent. Melting temperatures were determined by means of a microscope with a heated plate (Veb Kombinat, Nagema, Germany). Density measurements were performed at 20°C with a picnometer. Viscosimetric measurements were performed at 20°C with a Höppler viscometer (Veb Prüfgeräte Werk, Dresden, Germany). Nitrogen content was determined according to the Kjeldahl method.

IR spectra were recorded on a Specord M 80 (Carl Zeiss, Jena, Germany) spectrophotometer with KBr pellets. ¹H-NMR and ¹³C-NMR spectral analyses were performed at 300°K using an Avance DRX 400 (Bruker, Rheinstatten, Germany) instrument at 400 MHz (¹H) and 100 MHz (¹³C). Samples were analyzed in 5-mm tubes in CDCl₃. The spectra were referenced to internal TMS.

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

Dry tensile strength was measured according to Tappi Test Method T 404–87 and wet tensile strength according to Tappi Test Method T 456–87, using a commercial tensile tester.

Monomer synthesis

Synthesis of DAPK

Synthesis in toluene. DAPK was prepared by acid-catalyzed dehydrodecarboxylation of APA with the following procedure. In a four-neck flask (0.5 L) equipped with a thermometer, a mechanical stirrer, a Dean-Stark trap, and a N₂ inlet was charged with APA (190 g, 0.5 mol) and toluene (100 g); purged with a N₂ stream; heated with stirring up to boiling temperature of the resulting mixture (112°C), and refluxed over a period of 30 min. Toluene was used as solvent and carrier. TSA (1.9 g, 1.0 wt % referred to APA weight) was added and refluxing was continued for another 15 min. About 0.5 mL of water was collected as humidity of the reactants. Then, the reaction temperature was increased to 200°C by a gradual and slow (2.5 h) removal of toluene (about 65 g) from the system. At

this moment the release of some micromolecular reaction products (water and carbon dioxide) was observed. A high enough reaction rate was reached only at temperatures placed in the range 210–215°C. After 2.5 h, the release of both micromolecular products practically stopped. The reaction was finished during the next 30 min, when the traces of solvent and gases were removed by N₂ entrainment. Finally, 173 g of crude product (AN = 173 mg of KOH/g) and 6.1 g of condensation water were obtained.

The cooled reaction mixture was dissolved in diethyl ether. The removal of unreacted APA and the catalyst was made by filtration and repeated (twice) washing of the solution with distilled water. The reaction product was separated from the diethyl ether solution (after a preliminary concentration) by precipitation with petroleum ether and purified by redissolution into diethyl ether and reprecipitation into petroleum ether. A total of 121 g (63.7%) of purified DAPK (AN = 165 mg of KOH/g) was obtained.

Synthesis in DPK. DPK (75.0 g, used as reaction medium) and APA (106.0 g, 0.28 mol) were heated under stirring and a weak N₂ stream up to 160°C to give a homogeneous liquid solution. At this temperature, TSA (1.06 g, 1.0 wt % add, referred to APA weight) was added. No thermal effect was observed. After the homogenization of the reaction mass, temperature was increased up to 200°C during the next 30 min. At this temperature the dehydrodecarboxylation reaction started off. The reaction temperature was kept in the range 205–215°C for 2.5 h. In the course of the dehydrodecarboxylation reaction removal of the water was carried out, at the beginning by means of internal CO₂ stream and at the end by means of a weak stream of N₂. Because after a 2.5-h reaction duration the release of both gas and water ceased, heating was stopped. From synthesis 171 g of crude reaction mass (AN = 114 mg of KOH/g) and 3.5 g of condensation water were obtained.

The separation of DAPK from DPK was carried out by treatment with methyl alcohol of the powdered crude reaction mass. Low temperatures of up to -10 to -15°C favored the precipitation of DPK. Crude DAPK, achieved after the complete release of methyl alcohol (vacuum oven, 90°C, 6h), was dissolved into diethyl ether, filtered, washed two times with distilled water to remove unreacted APA and the catalyst, precipitated with petroleum ether, and again filtered. The purification of DAPK was finalized by washing on the filter with fresh petroleum ether to achieve a complete release of DPK. After being dried, 79.7 g (75.2%) of pure DAPK (AN = 161 mg of KOH/g) resulted.

Synthesis by cycloaddition reaction between AA and DPK. DPK (140.0 g, 0.25 mol) and AA (40.4 g, 0.5 mol + 10 wt % excess) containing 0.2 wt % hydroquinone were heated, under N₂ and stirring, at 140°C for 2 h, at 160°C for 2 h, and at 175°C for 1 h to give 173 g of

crude product. DAPK was separated from the reaction mass and purified in the same manner as described above when the dehydrodecarboxylation of APA in the presence of DPK was performed. Yield was 69.5 g (38.4%) of purified DAPK (AN = 160 mg of KOH/g).

Synthesis of DMPK

Synthesis in toluene. A mixture consisting of 202.0 g (0.5 mol) of MPA, 100 g of toluene, and 2.0 g (1.0 wt % add, referred to MPA weight) of TSA was processed as mentioned previously when DAPK was prepared in the presence of toluene. From this synthesis resulted 6.5 g of condensation water and 181 g of crude product which, after purification, yielded 113 g (55.9%) of purified DMPK (AN = 307 mg of KOH/g) as a yellow–orange solid material.

Synthesis in DPK. A mixture consisting of 75.0 g of DPK, 101.0 g (0.25 mol) of MPA, and 1.0 g (1.0 wt % referred to the weight of MPA) of TSA was processed as mentioned previously when DAPK was prepared by the dehydrodecarboxylation of APA in the presence of DPK to provide 4.1 g of condensation water and 91.5 g of crude product. After purification, 68.0 g (67.3%) of pure DMPK (AN = 298 mg of KOH/g) was obtained.

Synthesis by cycloaddition reaction between MA and DPK. DPK (140.0 g, 0.25 mol) and MA (54.5 g, 0.5 mol + 10 wt % excess) were heated under N₂ and stirring at 140°C for 2 h, at 160°C for 2 h, and at 170°C for 1 h. The crude reaction mass was processed as DAPK, synthesized by route (c), to give 89.0 g (45.8%) of purified DMPK (AN = 298 mg of KOH/g).

Polymer synthesis

Synthesis of poly(amide) (PA-1) and of poly(imide) (PI-1) at molar ratios ketone-diacid/TETA of 1:1

A four-neck flask (0.5-L capacity) provided with a thermometer, an ascendent condenser, a stirrer, and a N₂ inlet was charged with 140.0 g (0.2 mol) of DAPK or 150.6 g (0.2 mol) of DMPK, 30.1 g (0.2 mol) of TETA, and 50.0 g of *p*-xylene and purged, under stirring, with a weak N₂ stream. Because the reaction mixture presented a high chemical reactivity, a strong exothermal effect (approx. 20°C) was registered. After stabilization, the reaction temperature was increased to 120°C and kept at this level for 1 h to homogenize the reaction mass and to initiate the polycondensation process. Then a Dean-Stark separator was fitted to the flask and the reaction mixture was slowly heated over a period of 60 min. As a consequence of the gradual removal of the water–xylene mixture, the boiling temperature rose continuously up to 200°C. The polycondensation reaction was continued at this reaction temperature for 2 h. At the close, the reaction mass was

bubbled (15 min) with N₂ to release xylene and water traces, cooled, and purified. PA-1 was purified by precipitation of the trichloromethane solution into acetone and PI-1 by precipitation of *N,N*-dimethylformamide solution into methyl alcohol. Finally, 108.0 g (63.6%) of purified PA-1 or 140.1 g (77.5%) of purified PI-1 was obtained.

Synthesis of poly(amide) (PA-2) and of poly(imide) (PI-2) at molar ratios ketone-diacid/TETA of 1:1.5

A total of 140.0 g (0.2 mol) of DAPK or 150.6 g (0.2 mol) of DMPK, 45.2 g (0.3 mol) of TETA, and 60.0 g of *p*-xylene were processed in the same manner as mentioned previously. PA-2 was purified by extraction with hot cyclohexane and PI-2 by precipitation of trichloromethane solution into acetone to yield 156.7 g (84.6%) of purified PA-2 or 115.2 g (58.8%) of purified PI-2.

Synthesis of substituted polymers

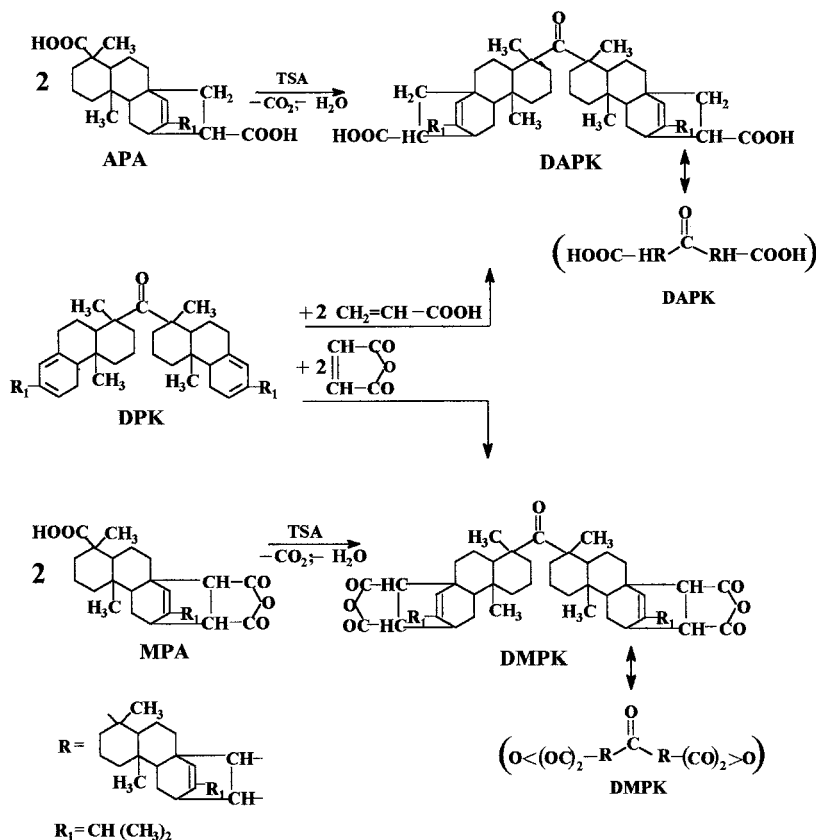
Finely grained polymer (0.05 mol) (39.8 g of PA-1, 42.6 g of PA-2, 42.4 g of PI-1, or 45.2 g of PI-2) was dissolved in 120 g of ethyl alcohol (PA-1 and PA-2) or 120 g of benzene (PI-1 and PI-2) by heating at 60°C. To the obtained PA-1 or PI-1 solutions 0.1 mol (9.3 g) of EC was added under stirring. To the PA-2 and PI-2 solutions 0.15 mol (14.0 g) of EC was added. In the next 5–7 min a weak exothermal effect (2–3°C) was observed. After stabilization, temperature was corrected to 75°C and maintained for the next 60 min. Finally, 166 g of substituted PA-1 solution (28.9 wt % solid content), 175 g of substituted PA-2 solution (32.1 wt % solid content), 169 g of substituted PI-1 solution (29.3 wt % solid content), or 176 g of substituted PI-2 solution (33.1 wt % solid content) was obtained.

RESULTS AND DISCUSSION

Monomer synthesis

Two new ketone-type monomers (DAPK and DMPK) were synthesized by the dehydrodecarboxylation of APA or MPA in the presence of a sulfonic-type catalyst (TSA) (Scheme 1).

Some specifications are noted in connection with the dehydrodecarboxylation procedure. Initially, toluene was used as an inert eluent, able to ensure, *inter alia*, a good stirring and a good homogeneity of the reaction mass. However, later, when the temperature must be rise and toluene was gradually removed, stirring slowed down because a part of the reaction mass showed an accentuate tendency to emerge from solution, even at elevated temperatures (150–160°C). This could be explained either by their limited solubility in toluene or by the formation of some reaction interme-



Scheme 1

diates with reduced solubilities in toluene. This last supposition seems more plausible because, carrying on the slow extraction of toluene, amazingly, it has been found that the reaction mass not only does not continued to solidify, but also becomes more and more fluid and stirring becomes easier and easier as a direct consequence of the chemical transformations that succeeded and ended in CO_2 and water release.

The fact that from the dehydrodecarboxylation of APA, carried out at reaction temperatures of up to $210\text{--}215^\circ\text{C}$, resulted in a ketone-diacid (DAPK) shows, on the one hand, that only the more labile carboxylic groups were involved in the reaction, namely that belonging to the levopimaric segment, and, on the other hand, that the two carboxylic groups of APA present different chemical reactivities. This last observation was also mentioned on other occasions.^{4,21}

Experimentally it was found that the above troubles regarding the dehydrodecarboxylation of APA or MPA in toluene could be avoided using DPK, the product of dehydrodecarboxylation of PA, as the reaction medium.¹⁹ This time, the reaction mass kept its homogeneity for the whole duration of the synthesis and the period of heating from 150 to $200\text{--}205^\circ\text{C}$ came down to only 30 min. The removal of condensation water was carried out by means of a weak N_2 stream.

DAPK and DMPK were also synthesized by cycloaddition of acrylic acid or maleic anhydride, as

dienophiles, to DPK (Scheme 1). This time, the transformation yields were much lower compared with that registered at the dehydrodecarboxylation of APA or MPA (Table I). In all probability, the best synthesis conditions were not used, although it was also possible, as from the coupling reaction, for some products of the monoaddition of dienophiles to DPK to arise. These were undesirable because, on the one hand, they decreased the production, separation, and purification yields of the double added ketones and, on the other hand, they were unusable as condensation monomers.

As a rule, the separation and the purification of the useful reaction products were carried out taking into account the fact that DAPK and DMPK, provided with acid functional groups, will dissolve into the solvents in which DPK, free of such groups, is insoluble (e.g., methyl alcohol, ethyl alcohol) and, on the contrary, will not dissolve into the solvents in which DPK dissolves (e.g., petroleum ether). The greatest yields of purified ketones were obtained when the route of dehydrodecarboxylation of APA, or MPA, in DPK (reaction medium) was used (Table I).

The purified DAPK and DMPK were yellow-orange solids that were soluble in diethyl ether, acetone, trichloromethane, 1,2-dichloroethane, methylene chloride, ethyl acetate, benzene, toluene, and *N,N*-dimethylformamide, slightly soluble in cyclohexane, and in-

TABLE I
Characterization Data of DAPK and DMPK

Characteristic	DAPK	DMPK
State	Solid	Solid
Conversion (%) ^a	63.7 ^b 75.2 ^c 38.4 ^d	55.9 ^b 67.3 ^c 45.8 ^d
Density (g/cm ³)	1.058	1.073
Melting point (°C)	121 ^c 117 ^d	137 ^c 127 ^d
AN (mg of KOH/g)	165 ^b 161 ^c 160 ^d (163.2) ^e	307 ^b 298 ^c 298 ^d (303.5)
Elemental analysis: C (%) ^c	77.67 (78.70)	75.74 (76.40)
Elemental analysis: H (%) ^c	9.70 (9.62)	8.30 (8.40)
Molecular weight, M_n ^{c,f}	725 (686)	782 (738)
Color	Yellow	Yellow–orange
Purity (%) ^{c,g}	98.6	98.2

^a Percentage of conversions determined from the weight of purified products referred to the weight of reactants.

^b Synthesized by dehydrodecarboxylation in toluene.

^c Synthesized by dehydrodecarboxylation in DPK.

^d Synthesized by cycloaddition reaction.

^e Calculated values are in parentheses.

^f Vapor pressure lowering method, trichloromethane, 45°C, benzil as standard.

^g Determined from AN found/ AN calculated.

soluble in petroleum ether, for which the main physicochemical characterization data are presented in Table I.

As shown in Scheme 1, the products resulting from the dehydrodecarboxylation of APA and MPA present, besides the ketone group, two carboxy groups (DAPK) or two anhydride groups (DMPK). Their structure was confirmed by both the data of physicochemical analysis (elemental analysis, acid number, and molecular weight, Table I) and the data of spectral analysis (Figs. 1 and 2).

It should be mentioned that because the IR spectra of the dehydrodecarboxylation products obtained by the various preparation routes did not significantly differ from each other, in Figure 1 only the IR spectra of DAPK and DMPK prepared by the dehydrodecarboxylation of APA and MPA are presented. In the IR spectrum of DAPK the characteristic bands are observed at 1735 cm⁻¹ ($\nu_{C=O}$ in ketones), 1700 cm⁻¹ ($\nu_{C=O}$ in COOH), 1470 cm⁻¹ (double bonds in hydrophenanthrene moiety), 1185 cm⁻¹, and 1260 cm⁻¹ (ν_{C-C} and δ_{C-C} in ketones). The IR spectrum of DMPK shows characteristic signals at 1850 and 1780 cm⁻¹ ($\nu_{C=O}$ in cyclic anhydride group), 1720 cm⁻¹ ($\nu_{C=O}$ in ketones), 1470 cm⁻¹ (double bonds in hydrophenanthrene moiety), 1190 and 1245 cm⁻¹ (ν_{C-C} and δ_{C-C} in ketones), and 1095 cm⁻¹ (ν_{C-O} in anhydrides).

The chemical transformation of COOH groups into ketone groups is evidenced by IR spectroscopy for both DAPK and DMPK. Indeed, the comparative examination of their spectra and of that of their acid precursors²¹ reveals the disappearance of the absorption band at 1700 cm⁻¹, characteristic of COOH groups, and the appearance of the absorption bands at 1735 cm⁻¹ (DAPK) or 1720 cm⁻¹ (DMPK), characteristic of ketone groups. However, in the case of DAPK the disappearance of the absorption band characteristic of COOH group cannot be really observed because of the existence of the other two, nonparticipant to the reaction, carboxylic groups, belonging to the acrylic segment.

The aforementioned ascertainments remain valid when the ¹³C-NMR spectra (Fig. 2) have been examined.

Thus, in the spectrum of DAPK (Fig. 2a) the ketone carbon resonates at 185.1 ppm, whereas in the spectrum of DMPK (Fig. 2b) the corresponding resonance signal appears at 186.2 ppm. The resonance signals at 178.3 ppm in the spectrum of DAPK and at 172.1 ppm in the spectrum of DMPK are due to carboxyl and anhydride carbons, respectively. The groups of signals at 146.6–123.8 ppm in the spectrum of DAPK and at 145.5–123.4 ppm in the spectrum of DMPK arise from unsaturated carbons of the hydrophenanthrene moieties. The signal ranges, 16.1–59.7 ppm for DAPK and 10.7–52.3 ppm for DMPK, are assigned to the methyl, methylene, methyne, and quaternary carbons from the acrylopimanic (maleopimanic) rest.

The data of thermogravimetric analysis concerning DAPK and DMPK presented in Figure 5 (curves a and b) and Table V (rows 1 and 2) show that these ketones, or rather ketone-diacids, can be considered fairly thermostable substances. For instance, their DT₀ data, considered a criterion of thermostability, fall into the range of 190–195°C. The melting point data inserted in Table I show values of 117 and 121°C for DAPK and values of 127 and 137°C for DMPK, in accordance with the used synthesis route. The smaller values registered for the cycloaddition products can be ascribed to the existence of some small quantities of products of partial addition of dienophiles (AA or MA) to DPK.

On the other hand, if the above values are compared with the melting point of DPK, found to be 67°C,¹⁹ it has been ascertained that the first are much higher. This last finding can be ascribed to the insertion of acid or anhydride groups into the starting structure of DPK.

But, besides this, these groups still provide to DAPK and DMPK a high chemical reactivity, which recommends them as monomers for polycondensation reactions.

Polymer synthesis

DAPK and DMPK were polycondensed with polyalkylenepolyamines (TETA) to investigate their behav-

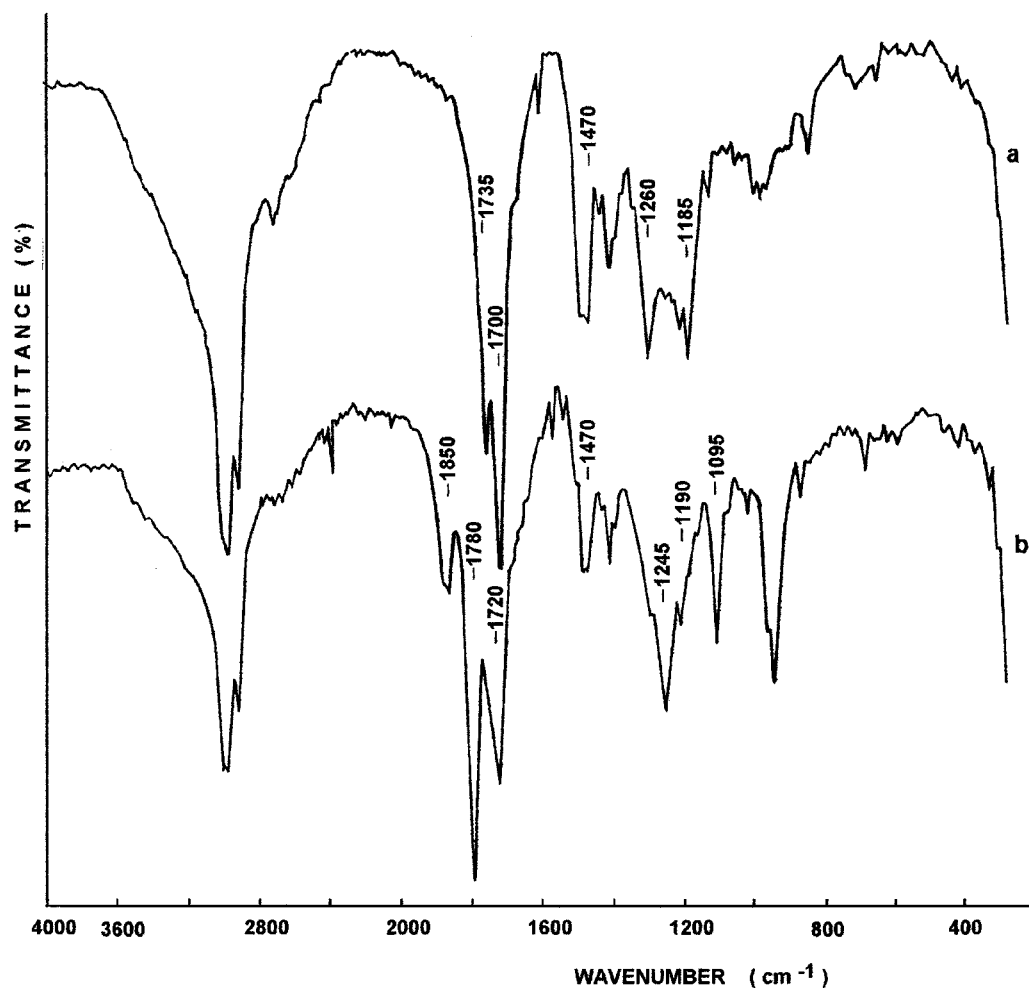


Figure 1 IR spectra of (a) DAPK and (b) DMPK.

ior as polycondensation monomers. The choice of TETA as comonomer was justified by reasons such as simplicity of the reaction, usefulness of the reaction products, and the possibility of undertaking a comparative study between the properties of these poly-(amide)s and poly(imide)s and that of the polymers resulting from the condensation of the same TETA with APA or MPA.²¹

Taking into account the fact that, besides carboxylic groups, ketone groups from DAPK and DMPK can also react with the primary amine groups from TETA, it follows that at molar ratios between the reactants of 1:1 some secondary amine groups ought to be involved into the condensation reaction. Intending to avoid this trouble, we extended the range of molecular ratios between TETA and DAPK or DMPK from 1:1 to 1.5:1. By this we created possibility for both the ketone groups and the carboxy groups to react solely with primary amine groups and, at the same time, to ascertain the influence exerted by the newly formed azomethine groups upon the properties of resulting polymers.

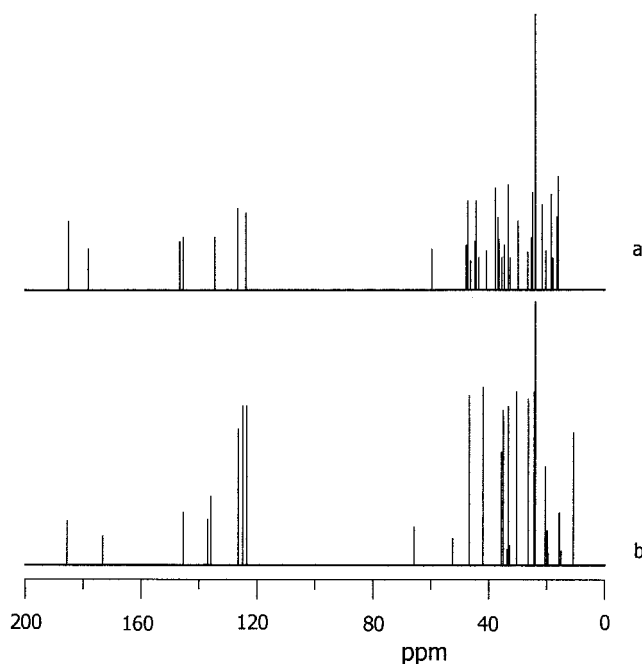
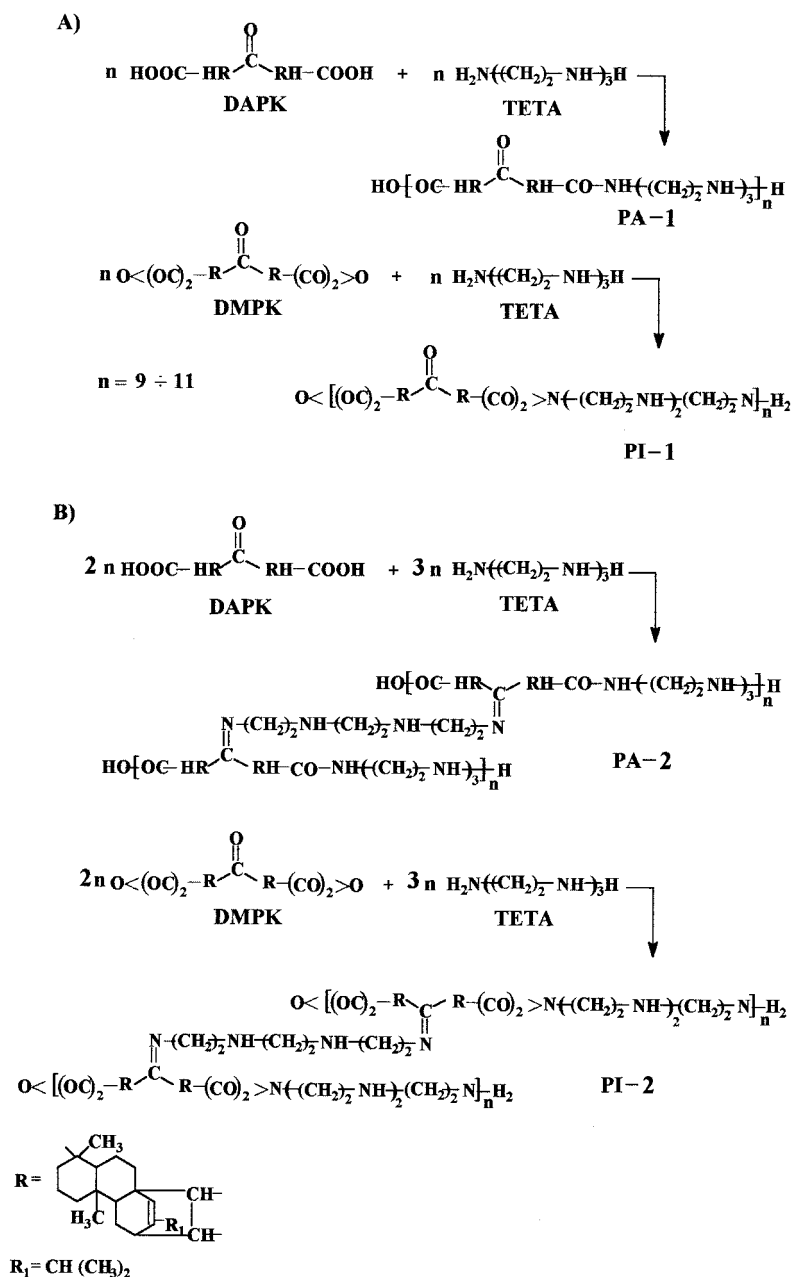


Figure 2 ¹³C-NMR spectra of (a) DAPK and (b) DMPK.



Scheme 2

The chemical structure proposed for the four products obtained by the polycondensation of the two ketone-diacids with TETA is shown in Scheme 2.

The elemental analysis and molecular weight data shown in Table III uphold the existence of poly-(amide)s and poly(imide)s presented in Scheme 2. The spectral analyses also confirm the presence of these polymers. Thus, in the IR spectra of PA-1 and PA-2, (Figure 3a and b) the characteristic bands are observed at 3400 (ν_{NH} in amides and amines), 1650 ($\nu_{\text{C}=\text{O}}$ in amides), and 1560 cm^{-1} ($\delta_{\text{N-H}}$ and $\nu_{\text{C-N}}$ in amides). The presence of the absorption band at 1730 cm^{-1} in the spectrum of PA-1 proves the existence of untrans-

formed ketone groups in its chemical structure. The disappearance of this band from the spectrum of PA-2 shows that, this time, the reaction between the ketone groups and the primary amine groups took place. In this latter case, it an absorption band at 1670 cm^{-1} ($\nu_{\text{C}=\text{N}}$) should have appeared, characteristic of azomethine groups, but this overlapped the band at 1650 cm^{-1} ($\nu_{\text{C}=\text{O}}$ in amides) forming together a wider and more intense band.

In the IR spectra of PI-1 and PI-2 (Figure 3c and d) the characteristic bands are observed at 3450 (ν_{NH} in amines), 1770, and 1700 cm^{-1} ($\nu_{\text{C}=\text{O}}$ in imides) and 1350 and 1400 cm^{-1} ($\nu_{\text{C-N}}$ in imides). In the spectrum

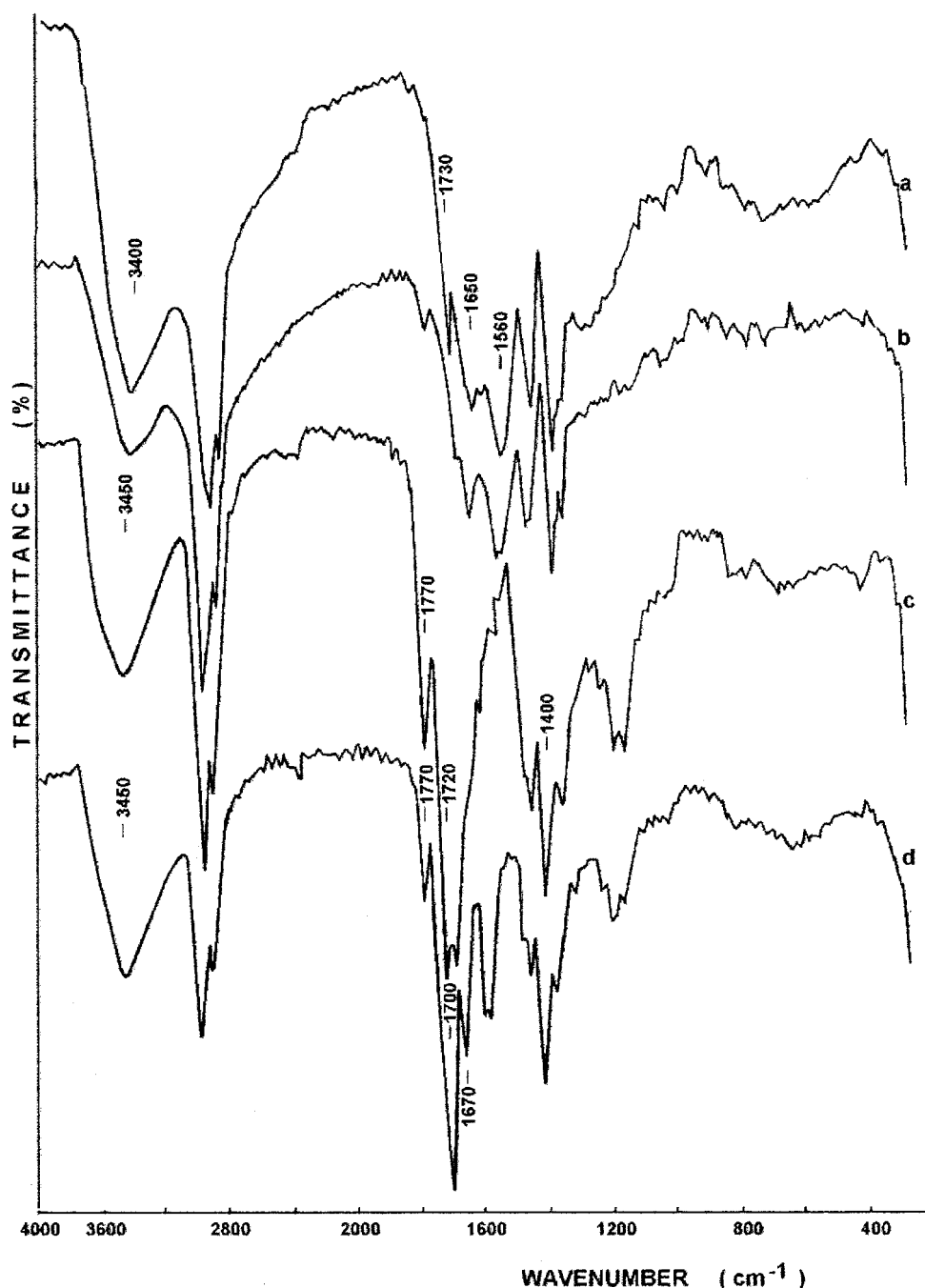


Figure 3 IR spectra of (a) PA-1, (b) PA-2, (c) PI-1, and (d) PI-2.

of PI-1 the absorption band at 1720 cm^{-1} , characteristic of ketone groups, forms a broad band together with the band at 1700 cm^{-1} . In the spectrum of PI-2 the disappearance of the band at 1720 cm^{-1} and the appearance of the band at 1670 cm^{-1} show that the transformation of ketone groups from DMPK into azomethine groups took place. Therefore, the IR data prove that in the polymers synthesized at molar ratios between the reactants of 1:1 the ketone groups remained practically unmodified, whereas in the polymers obtained at molar ratios TETA/ketone-diacid of

1.5:1 these were wholly transformed into azomethine groups.

The $^1\text{H-NMR}$ spectra (Fig. 4) are typical of polymer substances, because these are formed from some weak, broad bands. In these spectra one can remark upon the appearance of the peaks specific to amide (imide) protons. Thus, in the spectrum of PA-1 (Fig. 4a) the broad peak centered at 2.95 ppm is due to the protons of the methylene group attached to the amide carbonyl carbon atom and that centered at 3.55 ppm to the protons of the methylene group attached to the

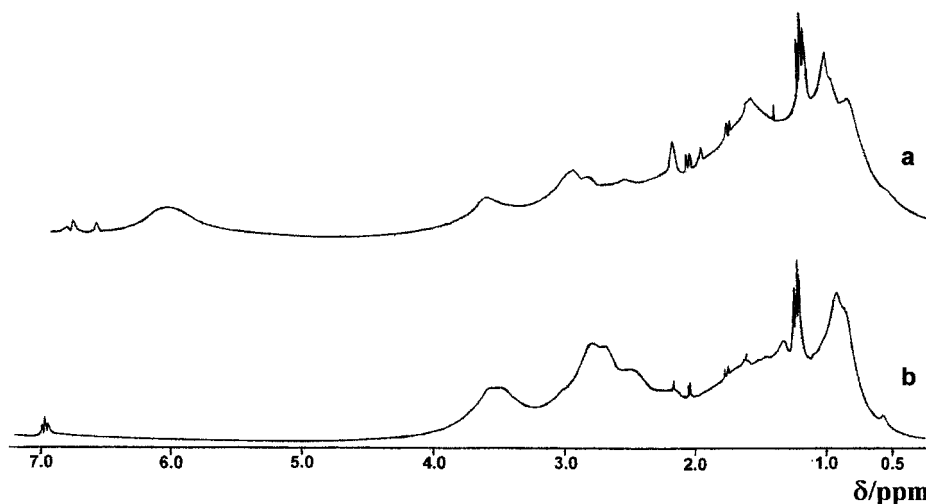


Figure 4 $^1\text{H-NMR}$ spectra of (a) PA-1 and (b) PI-1.

amide nitrogen atom. The aromatic pattern in the chemical shift range 6.7–7.0 ppm arises from the unsaturation of hydrophenanthrene moiety. The band at 6.06 ppm represents the secondary amide protons. In the spectrum of PI-1 (Fig. 4b) the corresponding peaks are at 2.85, 3.45, and 6.9–7.1 ppm, respectively. The absence in this spectrum of the peak due to secondary amide protons confirms that PI-1 is a polyimide. Because the $^1\text{H-NMR}$ spectra of PA-2 and PI-2 were similar to those of PA-1 and PI-1, the former are not presented in Figure 4.

The polymers obtained by the condensation of DAPK, or DMPK, with TETA are hard, brittle, solid materials, of brown or dark-brown color. Their solubilities are presented in Table II. Other characterization data are included in Table III.

As observed in Table III, the poly(amide)s and poly(imide)s are low molecular weight (MW) polymers.

TABLE II
The Solubility in Organic Solvents of the Crude Polycondensation Products^a

Solvent	PA-1	PA-2	PI-1	PI-2
Benzene	–	+–	+	+
Toluene	–	+–	+	+
Xylene	–	+–	+–	+
Acetone	–	–	–	–
<i>N,N</i> -dimethylformamide	+	+	+	+
Ethyl acetate	–	–	–	–
Diethyl ether	–	–	–	–
Methyl alcohol	+	+	–	+–
Ethyl alcohol	+	+	–	+–
Trichloromethane	+	+	+	+
Methylene chloride	+	+	+	+
Cyclohexane	–	–	–	–
Petroleum ether	–	–	–	–

^a +, Soluble; +–, partially soluble; –, insoluble.

The average degrees of polymerization, calculated taking into consideration the MW of the four structural units are (796 g/mol for PA-1, 851 g/mol for PA-2, 848 g/mol for PI-1, and 903 g/mol for PI-2), placed in the range 9.2–11.3. Drawing a parallel between these results and those achieved when the polymers obtained from the polycondensation of APA, or MPA, with TETA were analyzed,²¹ it comes out that, this time, the average polymerization degrees are somewhat greater, although the MW of structural units rose, practically doubled, too. This finding could be ascribed to the greater chemical reactivity of DAPK

TABLE III
Physicochemical Characterization Data of PA-1, PA-2, PI-1, and PI-2 (Purified Products)

Characteristic	PA-1	PA-2	PI-1	PI-2
State	Solid	Solid	Solid	Solid
Density (g/cm ³)	1.120	1.118	1.174	1.166
Elemental analysis:				
C (%)	77.23 (76.88) ^a	75.69 (76.14)	74.35 (75.00)	73.96 (74.42)
Elemental analysis:				
H (%)	8.93 (10.05)	9.88 (10.22)	8.87 (8.96)	9.32 (9.19)
Elemental analysis:				
N (%)	6.96 (7.03)	9.75 (9.87)	6.85 (6.60)	8.98 (9.30)
Molecular weight				
M_n^b	7825	8360	7790	10220
Melting range (°C)	190–194	172–175	260–264	207–210
Conversion (%) ^c	63.6	84.6	77.5	58.8
Color	Brown	Brown	Dark brown	Dark brown

^a Calculated values are in parentheses.

^b Vapor pressure lowering method, trichloromethane, 45°C, benzil as standard.

^c Percentage of conversions determined from the weight of purified products referred to the weight of reactants.

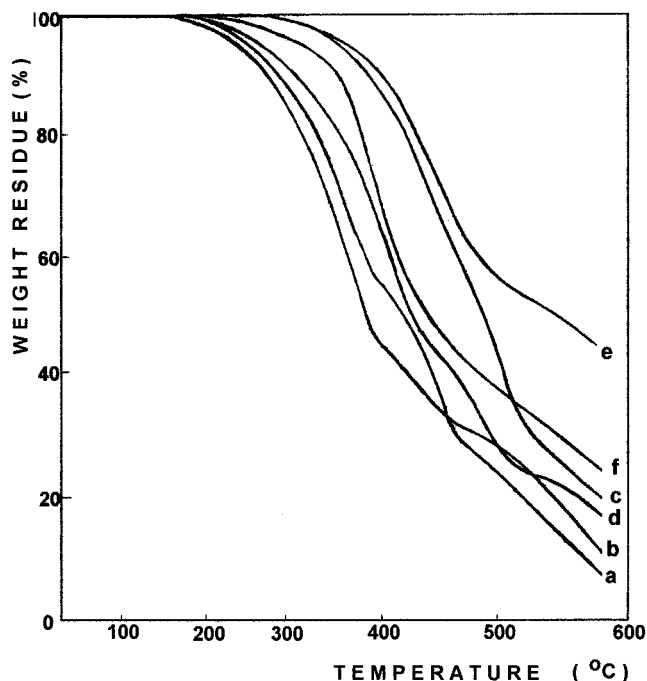


Figure 5 TGA curves of (a) DAPK, (b) DMPK, (c) PA-1, (d) PA-2, (e) PI-1, and (f) PI-2.

and DMPK compared with APA and MPA. The increased chemical reactivity can be a consequence of the fact that both DAPK and DMPK, unlike APA and MPA, present two perfectly identical acid functions. Otherwise, the increased chemical reactivity of DAPK and DMPK was already evidenced by the strong exothermal effect registered at the first contact between the comonomers.

The thermal behavior of the poly(amide)s and poly(imide)s was evaluated by TGA. Figure 5c, d, e, and f shows the thermograms of PA-1, PA-2, PI-1, and PI-2 and Table IV (rows 3–6) summarizes some thermal characterization data calculated from TGA curves.

As the results listed in Table IV show, the initial decomposition temperature (DT_0) was registered at 245°C for PA-1, 175°C for PA-2, 270°C for PI-1, and only 185°C for PI-2. If DT_0 is considered a criterion of thermostability, it follows that PA-1 and PI-1 present thermostabilities which are higher than that of the starting ketone-diacids and much higher than that of poly(amide) or of poly(amide-imide) resulting from the polycondensation of TETA with APA or MPA, respectively.²¹ The increase of thermostability could be ascribed, in the first case, to the formation of amide, or imide, linkages by polycondensation and in the second case to the presence of ketone linkages in the structure of PA-1 and PI-1.

At the same time, the data included in Table IV show that the polymers obtained at molar ratios TETA/ketone-diacid of 1.5:1 (PA-2 and PI-2) present a constant worse thermal behavior in comparison with

both polymers synthesized at equimolar ratios between the comonomers, and even with the starting ketone-diacids. This could be explained by the existence in the polymer chain structure of the azomethine linkages, (Scheme 2B), which are probably more susceptible toward the thermooxidative transformations. On the whole, the presented data prove that the investigated poly(amide)s and poly(imide)s behaved as fairly thermostable polymers, except PI-1, which behaved as a quite thermostable polymer.

The polymers obtained by the polycondensation of DAPK, or DMPK, with TETA, having in their structure free secondary amine groups, can be substituted with specific reactants, EC for instance. The substitutions have also been motivated by other reasons, such as the possibility to transform the polycondensation products into thermosetting, the ability to take over, and even to improve, the physicomechanical properties of the starting polymers; additional information concerning the possibility of the reaction between the ketone groups and the primary amine groups to take place, even at molar ratios TETA/ketone-diacid of 1:1. This last assertion, if real, should have to be confirmed by some smaller EC retention yields and, implicitly, by some properties of the resulting crosslinked polymers, e.g., the remanent solubility in methyl alcohol.

The syntheses of addition products of EC to PA-1, PA-2, PI-1, and PI-2 were carried out using the following reaction conditions:

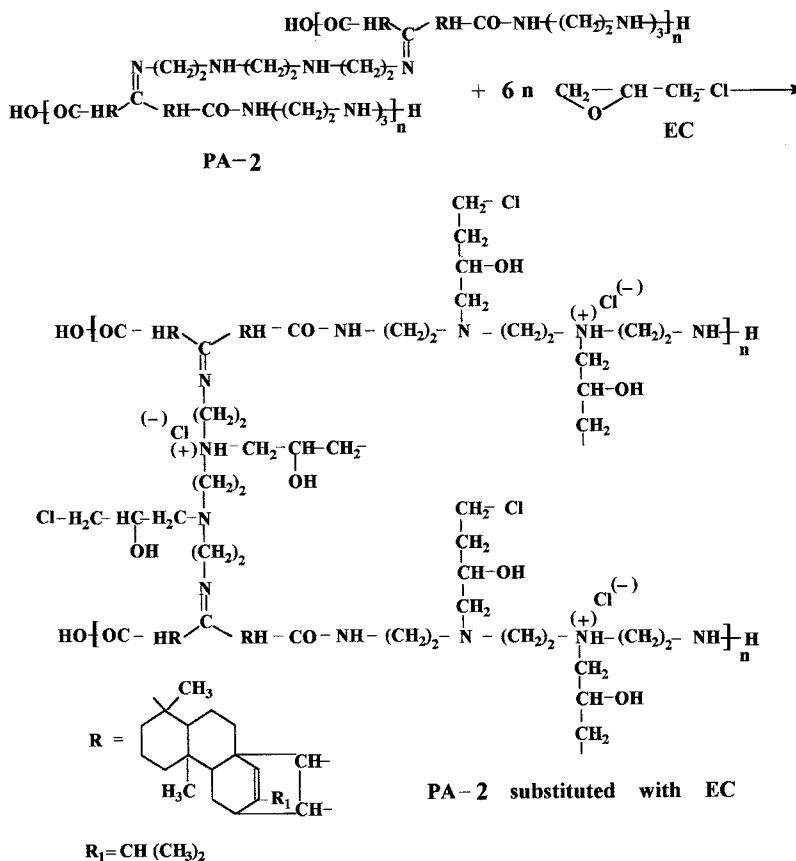
- molar ratio EC/TETA of 2:1;
- reaction temperature of 75°C;
- reaction duration of 60 min.

Proceeding in this manner, the advanced crosslinking of the substituted polymers was prevented, intending on the one hand, to keep the solubility of the reaction products in the solvents used as reaction medium and, on the other hand, to preserve enough possibilities of crosslinking during the subsequent postthermal treatments.

TABLE IV
Thermal Properties of Synthesized Pimaryl Ketones and Polymers^a

Analyzed product	DT_0 (°C)	DT_{10} (°C)	WL_{500} (%)
DAPK	195	290	77
DMPK	190	280	71
PA-1	245	340	68
PA-2	175	275	78
PI-1	270	360	49
PA-2	185	340	68

^a DT_0 , initial decomposition temperature; DT_{10} , decomposition temperature at 10% weight loss; WL_{500} , weight loss at 500°C.



Scheme 3

The chemical structure proposed, for example, for the reaction product between EC and PA-2 is presented in Scheme 3. One can observe the existence of both hydroxypropylic bridges and propylenechlorohydrine segments on the polymer chain. The former are responsible for the quaternization of the tertiary amine groups, whereas the latter represent the places on the polymer chain that will participate in the complete crosslinking of the polymer after removal of the solvent.

The proposed structure is confirmed by the IR spectra of crosslinked polymers, shown in Figure 6. In the spectra of PA-1 and PA-2 one notices the change of the absorption band at 3400 cm^{-1} from one sharp peak (Fig. 3a and b), characteristic of NH groups, into one wide curve (Fig. 6a and b), characteristic of OH groups. This transformation reflects, on one hand, the consumption, by reaction with EC, of the secondary amine groups and, on the other hand, the appearance of the hydroxy groups, by opening of the epoxy rings. The disappearance of the band at 1560 cm^{-1} (δ_{NH}) from the IR spectra of PA-1 and PA-2 and the appearance of the absorption bands at $1180\text{--}1250 \text{ cm}^{-1}$ ($\nu_{\text{C-N}}$ in amines) in the IR spectra of PA-1 and PA-2 substituted with EC evidence the transformation of secondary amine groups into tertiary groups as a result of the

substitution. The absence of absorption bands characteristic of C-Cl linkage from the spectra of PA-1 and PA-2 substituted with EC can be ascribed to the advanced crosslinking degree reached by these products.

On the whole, the above findings remain valid when the IR spectra of PI-1 and PI-2 are examined, too. But, this time one can remark upon the presence of the absorption bands at $635\text{--}690 \text{ cm}^{-1}$ ($\nu_{\text{C-Cl}}$), which denotes the existence of propylenechlorohydrine segments on the polymer chain and, implicitly, a less advanced crosslinking of these polymers.

Some properties of the solutions of the polymers substituted with EC are listed in Table V.

As can be seen from the data listed in Table V, the poly(amide) synthesized at a molar ratio ketone-diacid/TETA of 1:1 (PA-1) presents a somewhat smaller EC retention yield compared with that achieved when molar ratios of 1:1.5 were used (PA-2 and PI-2). This can be a consequence and at the same time new proof in favor of the supposition according to which the reaction between the ketone groups and the primary amine groups could take place not only at molar ratios of 1:1.5, but also at equimolar ratios between the comonomers. Under such conditions, a small part of the secondary amine groups supplied the deficit of the primary amine groups in the amidation reaction

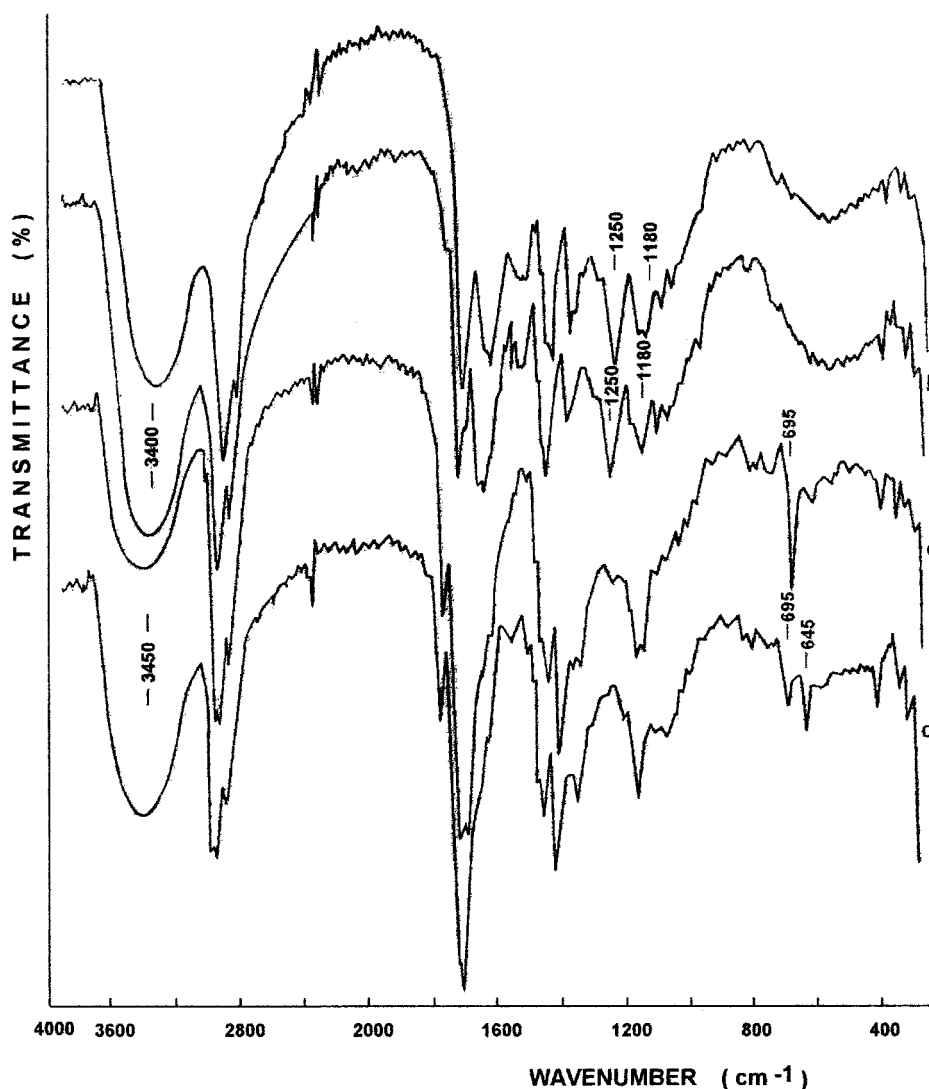


Figure 6 IR spectra of crosslinked (a) PA-1, (b) PA-2, (c) PI-1, and (d) PI-2.

(Scheme 4) and the number of secondary amine groups available for the subsequent reaction with EC diminished. As a result, EC retention yield decreased.

TABLE V
Characterization Data of PA-1, PA-2, PI-1,
and PI-2 Substituted with EC

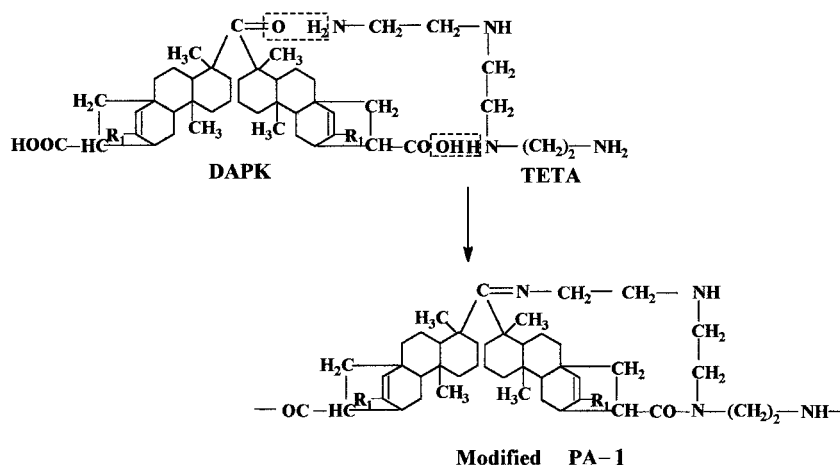
Characteristic	PA-1	PA-2	PI-1	PI-2
Initial solutions				
Concentration (wt %)	24.91	26.20	26.11	27.36
Viscosity (mPa · s)	8.03	4.84	6.83	9.76
Final solutions				
Concentration (wt %)	28.90	32.10	29.30	33.10
Viscosity (mPa · s)	9.56	6.23	10.60	16.53
EC retention yield (%) ^a	76.85	96.93	88.96	93.26
Gelation time (days)	>120	>120	102	35

^a Calculated from the concentration data of the final solutions (approximate values).

To the above we can also add the fact that PA-1 presented a certain solubility in methyl alcohol, even after a prolonged postthermal treatment (90 min, 100°C). An extraction yield of 83.6 wt % was registered. The phenomenon can be ascribed to a weaker polymer crosslinking caused, in turn, by the same diminution of the amount of EC retained on the polymer chains.

Because the reaction presented in Scheme 4 could not take place when a poly(imide) was synthesized at a molar ratio of 1:1 (PI-1), all secondary amine groups remained available for the substitution with EC and the EC retention yield rose to 88.96%.

The state of things was quite different when molar ratios of 1:1.5 were used (PA-2 and PI-2). This time, there were enough primary amine groups for both the reaction with ketone groups and the reaction with carboxy groups. As such, the number of secondary



Scheme 4

amine groups available for the substitution with EC was not affected, the EC retention yield was maximized, the crosslinking degree of the polymers rose, and the solubility in organic solvents (methyl alcohol, benzene) decreased, tending to zero.

The substituted polymers are thermosetting substances that, after the thermal posttreatment, transform into crosslinked, insoluble, infusible, hard, and dark-brown materials. Such an observation immediately suggested their utilities as consolidation agents for fibrous cellulosic, or noncellulosic, networks. Indeed, it was found experimentally that the initial dry tensile breaking strength of a common cellulose filter paper ($\sigma_{\text{initial}} = 1.37 \text{ N/cm}$) rose with 24.8% ($\sigma = 1.71 \text{ N/cm}$) after an impregnation with 5 wt % of PI-1 substituted with EC and with 55.5% ($\sigma = 2.13 \text{ N/cm}$) after an impregnation with 10 wt %, both referred to the weight of the starting paper. It was also observed that the filter paper impregnated with 10 wt % PI-1 substituted with EC presented a certain (approx. 10%, referred to dry tensile strength) wet tensile strength. This was imparted, inter alia, by the water repellency of crosslinked polymer, due, in turn, to the presence of hydrophenanthrene moieties, well known as hydrophobicity promoters, in the polymer structure.

CONCLUSION

Two new ketone-type derivatives of Diels–Alder adducts of levopimaric acid with acrylic acid and maleic anhydride were synthesized and characterized. The syntheses were carried out by both the dehydrodecarboxylation of acrylic or maleic adducts in presence of sulfonic-type acid catalysts and the cycloaddition of acrylic acid, or maleic anhydride, to dipimaryl ketone. The ketone derivatives, in fact ketone-diacids, were polymerized by polycondensation with polyalkylene-polyamines. Low MW poly(amide)s, or poly(imide)s,

were obtained. The substitution with EC of the secondary amine groups led to three-dimensional, thermosetting polymers. These were suitable for special purposes, e.g., for the consolidation of the materials with network fibrous structures. The poly(imide)s, rather than poly(amide)s, turned out to be substances with good thermostability.

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