

# Aromatic–Aliphatic Acrylic Monomers and Polymers: Synthesis and Characterization

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**ABSTRACT:** Two new ester-type monomers were synthesized by the condensation of acrylic acid with the products of the hydroxyethylation of 4-nonylphenol or 4-*tert*-butylphenol. The hydroxyethylation reaction was performed with 1,3-dioxolan-2-one in the presence of alkalies. By hydroxyethylation, the phenols were changed into alcoholic derivatives able to react with acrylic acid to give acrylic esters. The insertion of the aryl–alkyl groups into the structure of the acrylic esters, and implicitly of the corresponding polymers, was carried out with the intention of increasing their thermostability and improving their behavior as pressure-sensitive adhesives on the whole. The monomers and the polymers were characterized by elemental and thermogravimetric analyses, IR and <sup>1</sup>H-NMR spectroscopy, and other special methods. The results of these investigations confirmed the formulated suppositions. The inherent viscosities of the resulting polymers were in the range of 47–64 mL/g, and their thermal stability was up to 315–320°C, far higher than that of the polyacrylates used. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 802–814, 2002

**Key words:** adhesives; polyesters; radical polymerization; thermal properties

## INTRODUCTION

The homopolymers of acrylic esters and their copolymers with other various acrylic or vinylic monomers are well-known as self-adhesive compounds with remarkable tack, adhesion, and cohesion properties. For this reasons, they have been widely used in the most varied fields of human activity, including instruction and domestic activity and medicine, electronics, car building, and aeronautics.<sup>1–5</sup> The synthesis, characterization, and especially the directions for use of these polymers have been discussed in detail in the literature.<sup>6–23</sup>

As a rule, acrylic monomers are esters of acrylic or methacrylic acids with the most com-

mon alcohols as methyl, ethyl, butyl, octyl, 2-ethylhexyl, nonyl, isononyl, decyl, cyclohexyl, and even C<sub>14</sub>–C<sub>20</sub> alcohols, although some particular acrylic esters such as glycidyl (meth)acrylate, cyanoethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, hydroxypropyl-acrylate, ethylene glycol (meth)acrylate, polyethylene glycol di(meth)acrylate, trimethylol propane triacrylate, isobornil acrylate, and phenylhydroxypropyl acrylate, identically widespread, exist too.<sup>24–38</sup> Because acrylic homopolymers are sometimes deficient in either adhesiveness or cohesiveness, copolymerization with polar comonomers or mixture with various reactive compounds has been used to improve these troubles.

With regard to the thermal behavior of acrylic copolymers, the literature specifies that the upper limit of the working temperature is about 235°C.<sup>1</sup> One attempt to overcome this limit was made when acrylic adhesives were modified by the ad-

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dition of phenolformaldehyde resins or epoxy resins prior to coating on the backing film.<sup>39-42</sup> However, this very interestingly appeared to introduce the elements responsible for an increase in thermal stability just into the chemical structure of acrylic esters. Thus, the insertion of aryl groups into the monomer or polymer structure is expected to improve their thermal behavior, and if the aryl structures are also substituted with alkyl groups (e.g., nonyl or *tert*-butyl), it is expected that the adhesive and cohesive properties of the subsequent polymers will also improve.

The introduction of aromatic nuclei into the chemical structure of acrylic esters by the esterification of phenols or their derivatives is difficult because of hard synthesis conditions. Another, more advantageous way to obtain acrylic esters with aryl structures in the composition is the transformation of the phenols into phenoxyethyl alcohols, which easily can condense, even with acrylic acid. Phenoxyethyl alcohols can be obtained either by treatment of the phenols with ethylene oxide<sup>43-51</sup> or 2-chloroethanol<sup>52-54</sup> or by hydroxyethylation with 1,3-dioxolan-2-one[ethylene carbonate (EC)] in the presence of alkalis. This last route was founded and used for a long time in organic synthesis.<sup>55-59</sup> Because this is a facile, specific, and perfectly controllable reaction that allows for the obtainment of unitary products (phenoxyethyl alcohols) at high yields, it was also used in this research.

The purpose of this article is to present the synthesis and polymerization of acrylic esters of 2-(4-nonylphenoxy)ethyl alcohol (NPEA) and 2-(4-*tert*-butylphenoxy)ethyl alcohol (BPEA). These acrylic monomers are acrylic acid 2-(4-nonylphenoxy)ethyl ester (NPPE) and acrylic acid 2-(4-*tert*-butylphenoxy)ethyl ester (BPPE). The monomers were homopolymerized or copolymerized with acrylic acid (AA) and/or acrylic acid 2-ethylhexyl ester (AEHE). The resulting polymers were characterized and tested as self-adhesive compounds. Because both alkyl structures and polar etheric and esteric linkages exist in the structure of these polymers, it is easy to anticipate some good performance as pressure-sensitive adhesives.

## EXPERIMENTAL

### Materials

4-Nonyl phenol (NPh; Fluka AG, Buchs, Switzerland, mixture with ~ 85% *p*-isomers) was purified just before use by repeated (twice) distillation

under vacuum (180°C, 20 hPa). 4-*Tert*-butyl phenol (BPh; Fluka, > 97%), AA (Fluka, > 99%), 1,3-dioxolan-2-one (Fluka, 99%), and toluene-4-sulfonic acid (TSA; Aldrich, Steinheim, Germany, > 99%) were used as received. The organic solvents used were analytical grade. Pyridine was distilled before use.

### Measurements

Acid number (AN) was determined with 0.1N aqueous KOH in the presence of phenolphthalein with acetone as a solvent. Hydroxy content (HC) was determined by esterification of the hydroxy groups with acetic anhydride in the presence of pyridine, according to ref. 60. Iodine number (IN) was determined with pyridine-sulfate-bromide (C<sub>6</sub>H<sub>5</sub>N · H<sub>2</sub>SO<sub>4</sub> · Br<sub>2</sub>), according to ref. 60.

Melting temperatures were determined by means of a capillary melting-point apparatus. Density measurements were performed at 20°C with a picnometer. Viscosimetric measurements were performed at 25°C with an Ubbelohde viscometer (inherent viscosity) or a Höppler viscometer (Vebe Prüfgeräte Verk, Dresden, Germany) (dynamic viscosity) and with acetone as a solvent.

IR spectra were recorded on a Specord M 80 (Carl Zeiss, Jena, Germany) spectrophotometer with KBr pellets. The <sup>1</sup>H-NMR spectra were recorded on a JEOL JNMC-60 HL (Tokyo, Japan) instrument with CDCl<sub>3</sub> as a solvent and tetramethylsilane as an internal reference. Thermogravimetric analysis (TGA) was carried out with a Paulik-Paulik-Erdey type Magyar Optical Plant-Budapest derivatograph in air at a heating rate of 12°C/min.

The adhesive strength of the pressure-sensitive products was determined with the standard adhesion test (180°-angle peel adhesion) and a pendulum-type tensile tester, as described in ASTM D-1000. Another method also used for testing of the adhesive properties was the 0°-angle hold test.<sup>61</sup> This test determines how long a 1 in. × 1 in. section of adhesive tape will support a 1,000 g weight under standard conditions. The two previously mentioned methods were selected because, together, they offer complementary information about the adhesive and cohesive strengths of the analyzed materials.

### Synthesis of Monomer Precursors

#### Synthesis of NPEA

In a 0.5-L-capacity reaction flask equipped with a stirrer, a nitrogen inlet, a thermometer, and a

Dean–Stark trap, 220 g (1 mol) of NPh and 97.8 g (1 mol + 10 wt % excess) of EC were introduced. Nitrogen was purged in the flask, and the reaction mixture was heated at 70°C for complete dissolution of the solid materials. The excess of EC was produced with the aim of achieving complete consumption of NPh and, thus, facilitating the purification of the reaction mass. The EC excess, unlike NPh, could be easily removed by an ordinary washing with distilled water.

The catalyst, an aqueous solution consisting of NaOH (1.0 g, 1 wt % referred to the weight of EC) and water (1.5 g) was introduced at 70°C and heating was continued under stirring up to 135°C. At this temperature, the release of carbon dioxide (bubbles) and water (small amounts resulting from the humidity of the reactants and from the catalyst solution) was noted. The release of carbon dioxide continued with a high enough rate at 140–145°C. After 3 h, the release of the gas practically stopped. The reaction was finished off at 150–155°C during the next 1 h.

The unreacted EC and the catalyst were removed from the crude product (268 g) by repeated (twice) washing with hot distilled water. Cyclohexane (100 g) was fed into the system for a better separation of the two liquid layers. After the mixture was separated into two phases by means a funnel, the upper layer was collected, filtered, and dried by the removal of the cyclohexane at reduced pressure. Finally, the resulting crude mass was distilled under vacuum to give 203 g (64%) of pure NPEA as a colorless, viscous liquid with a boiling point (BP) of 222°C/40 hPa.

ELEM. ANAL.: Calcd for  $C_{17}H_{28}O_2$  [molecular weight (MW) = 264] C, 77.27%; H, 10.61%. Found: C, 77.10%; H, 10.29%.

The IR spectrum exhibited absorptions at 3350  $cm^{-1}$  ( $\nu_{OH}$ ), 1425  $cm^{-1}$  ( $\delta_{OH}$ ), 1255  $cm^{-1}$  ( $\nu_{C-O}$  in  $C_{arom}-O-C$ ), 1120  $cm^{-1}$  ( $\nu_{C-O}$  in  $C_{aliph}-O-C$ ), 1045  $cm^{-1}$  ( $\nu_{C-O}$  in  $C_{aliph}-OH$ ), and 900 and 930  $cm^{-1}$  ( $\gamma_{OH}$  in primary alcohols).

$^1H$ -NMR ( $\delta$ , ppm, in  $CDCl_3$ ): 0.95 [s, 9H from  $-C(CH_3)_3$ ], 1.45 [s, 6H from  $-C(CH_3)_2-$ ], 1.7 [s, 4H from  $-(CH_2)_2-$ ], 3.45 [s, 4H from  $-O-CH_2-CH_2-$ ], 3.85 (s, 1H from OH), 6.40–6.70 (m, 2H ortho to ethoxy group), 6.75–7.15 (m, 2H ortho to nonyl group).

#### Synthesis of BPEA

A mixture consisting of 150 g (1 mol) of BPh and 97.8 g (1 mol + 10 wt % excess) of EC were processed in the manner mentioned previously.

From the synthesis, we obtained 198 g of crude product, which we purified by washing with hot distilled water, drying in the presence of cyclohexane, and distilling under vacuum. The yield was 155 g (62.8%) of colorless, viscous liquid with a BP of 186°C/40 hPa.

ELEM. ANAL. Calcd for  $C_{12}H_{18}O_2$  (MW = 194): C, 74.23%; H, 9.28%. Found: C, 73.95%; H, 9.03%.

The IR spectrum exhibited absorptions at 3360  $cm^{-1}$  ( $\nu_{OH}$ ), 1425  $cm^{-1}$  ( $\delta_{OH}$ ), 1255  $cm^{-1}$  ( $\nu_{C-O}$  in  $C_{arom}-O-C$ ), 1125  $cm^{-1}$  ( $\nu_{C-O}$  in  $C_{aliph}-O-C$ ), 1040  $cm^{-1}$  ( $\nu_{C-O}$  in  $C_{aliph}-OH$ ), and 880 and 910  $cm^{-1}$  ( $\gamma_{OH}$  in primary alcohols).

$^1H$ -NMR ( $\delta$ , ppm, in  $CDCl_3$ ): 1.25 (s, 9H from *tert*-butyl group), 3.25 (s, 4H from  $-O-CH_2-CH_2-$ ), 3.95 (s, 1H from OH), 6.50–6.75 (m, 2H ortho to ethoxy group), 6.85–7.15 (m, 2H ortho to *tert*-butyl group).

#### Monomer Synthesis

##### Synthesis of NPEE

Acrylic ester of NPEA was prepared by direct, acid-catalyzed condensation with the following procedure. In a three-necked flask (500 mL) equipped with a thermometer, a mechanical stirrer, a Dean–Stark trap, and a  $N_2$  inlet was charged with NPEA (135.4 g, 0.5 mol), AA (36.4 g, 0.5 mol), TSA (1.75 g, 1 wt % referred to the weight of the reactants), hydroquinone (0.10 g, 0.25 wt % referred to the weight of AA), and toluene (20 mL); purged with a  $N_2$  stream; and heated to the boiling temperature of the realized mixture (90°C). We removed water produced in the condensation reaction by entraining with toluene. After a condensation time of about 2 h, 14 mL of condense (water-entrained AA mixture) was collected, and as a direct consequence, the reaction temperature rose to 140°C.

At this moment, new amounts of AA (7.3 g, 20 wt % excess referred to the stoichiometric requirement) and TSA (0.5 g) were added, and heating was continued at 140–150°C for another 1 h to finish off the condensation and to ensure the complete consumption of NPEA. By this way, we created the preconditions necessary to obtain NPEE of high purity. Thus, NPEA, that of which NPEE hardly separated, did not disturbed the purification more and AA, the sole reactant remaining in excess, could be removed from the crude product by an elementary washing with distilled water.

Then, a Dean–Stark separator was substituted with a descendent condenser, and toluene was

extracted under vacuum. Finally, 163 g of crude NPEE was obtained.

NPEE was purified by dissolution in diethyl ether and washing (at least twice) with distilled water. After the removal of diethyl ether, the remaining NPEE was distilled under vacuum in the presence of hydroquinone to yield 118 g (65.1%) of pure NPEE as a colorless, medium viscous liquid with a BP of 222°C/13.3 hPa.

ELEM. ANAL. Calcd for  $C_{20}H_{30}O_3$  (MW = 318): C, 75.47%; H, 9.43%. Found: C, 75.57%; H, 9.26%.

The IR spectrum exhibited characteristic absorptions at  $1735\text{ cm}^{-1}$  ( $\nu_{C=O}$  in esters),  $1645\text{ cm}^{-1}$  ( $\nu_{C=C}$  in acrylics),  $1410\text{ cm}^{-1}$  ( $\delta_{CH}$  in acrylics),  $1060\text{ cm}^{-1}$  ( $\nu_{C-O}$  in unsaturated esters),  $980\text{ cm}^{-1}$  ( $\gamma_{CH}$  in acrylics), and 810 and  $835\text{ cm}^{-1}$  ( $\nu_{CH}$  in 1,4 disubstituted benzene).

$^1\text{H-NMR}$  ( $\delta$ , ppm, in  $\text{CDCl}_3$ ): 0.95 (m, 3H from  $\text{CH}_3$ ), 1.45 (m, 16 H from eight  $\text{CH}_2$  groups), 3.60–4.60 (m, 4H from  $\text{O-CH}_2\text{-CH}_2\text{-O}$  group), 5.60–6.40 (m, 3H from acrylic group), 6.40–7.25 (m, 4H from 1,4 disubstituted benzene ring).

### Synthesis of BPEE

A mixture consisting of 150 g (0.75 mol) of BPEA, 54.6 g (0.75 mol) of AA, 2.05 g (1 wt % referred to the weight of the reactants) of TSA, 0.14 g (0.25 wt % referred to the weight of AA) of hydroquinone, and 25 mL of toluene was processed as mentioned previously. From this synthesis, we obtained 20.6 g of condense (in fact, a  $\text{H}_2\text{O-AA}$  mixture) and 192 g of crude product, which after purification, yielded 139 g (64%) of pure BPEE as a colorless, medium viscous liquid with a BP of 205°C/40 hPa.

ELEM. ANAL. Calcd for  $C_{15}H_{20}O_3$  (MW = 248): C, 72.58%; H, 8.06%. Found: C, 72.27%; H, 8.18%.

The IR spectrum exhibited characteristic absorptions at  $1725\text{ cm}^{-1}$  ( $\nu_{C=O}$  in esters),  $1640\text{ cm}^{-1}$  ( $\nu_{C=C}$  in acrylics),  $1410\text{ cm}^{-1}$  ( $\delta_{CH}$  in acrylics),  $1065\text{ cm}^{-1}$  ( $\nu_{C-O}$  in unsaturated esters),  $975\text{ cm}^{-1}$  ( $\gamma_{CH}$  in acrylics), and 800 and  $825\text{ cm}^{-1}$  ( $\nu_{CH}$  in 1,4 disubstituted benzene).

$^1\text{H-NMR}$  ( $\delta$ , ppm, in  $\text{CDCl}_3$ ): 1.30 (s, 9 H from *tert*-butyl group), 3.95–4.60 (m, 4H from  $\text{O-CH}_2\text{-CH}_2\text{-O}$  group), 5.60–6.30 (m, 3H from acrylic group), 6.60–7.25 (m, 4H from 1,4 disubstituted benzene ring).

## Polymer Synthesis

### Synthesis of Poly(NPEE) or Poly(BPEE)

A 250-mL reaction flask equipped with a stirrer, a thermometer, an ascendent condenser, and a  $\text{N}_2$

inlet was charged with 97.4 g NPEE monomer (76.0 g BPEE, 0.3 mol), 30 g of solvent (benzene, cyclohexane), and 0.15 g (0.15 wt % added) of dibenzoylperoxide (DBP). The reaction mixture (76.5 wt % monomer) was heated under  $\text{N}_2$  up to 85°C for about 20–25 min, when polymerization started up and a weak exothermal effect was registered. After stabilization of the system, the heating of the reaction mass was continued under gentle reflux (115°C) for another 90 min. Because toward the end of this heating period the viscosity of the reaction medium appreciably rose, the medium was diluted by the addition of small amounts of solvent from time to time to maintain an efficient stirring. Finally, the polymerization was ceased by dilution with solvent, which this time was acetone. The polymer solution had a solid content of 50 wt %. The separation of the polymer from the solution, if desired, was carried out by precipitation with methanol and dried at 50°C under vacuum.

The same procedure was applied to the AEHE homopolymerization. The resulting polymer was used as a control when poly(NPEE) or poly(BPEE) were characterized.

### Copolymerization of NPEE (BPEE) with AEHE

NPEE or BPEE (36.0 g), 36.0g of AEHE, 28 g of cyclohexane, and 0.11 g (0.15 wt % addition) of DBP were processed as mentioned previously.

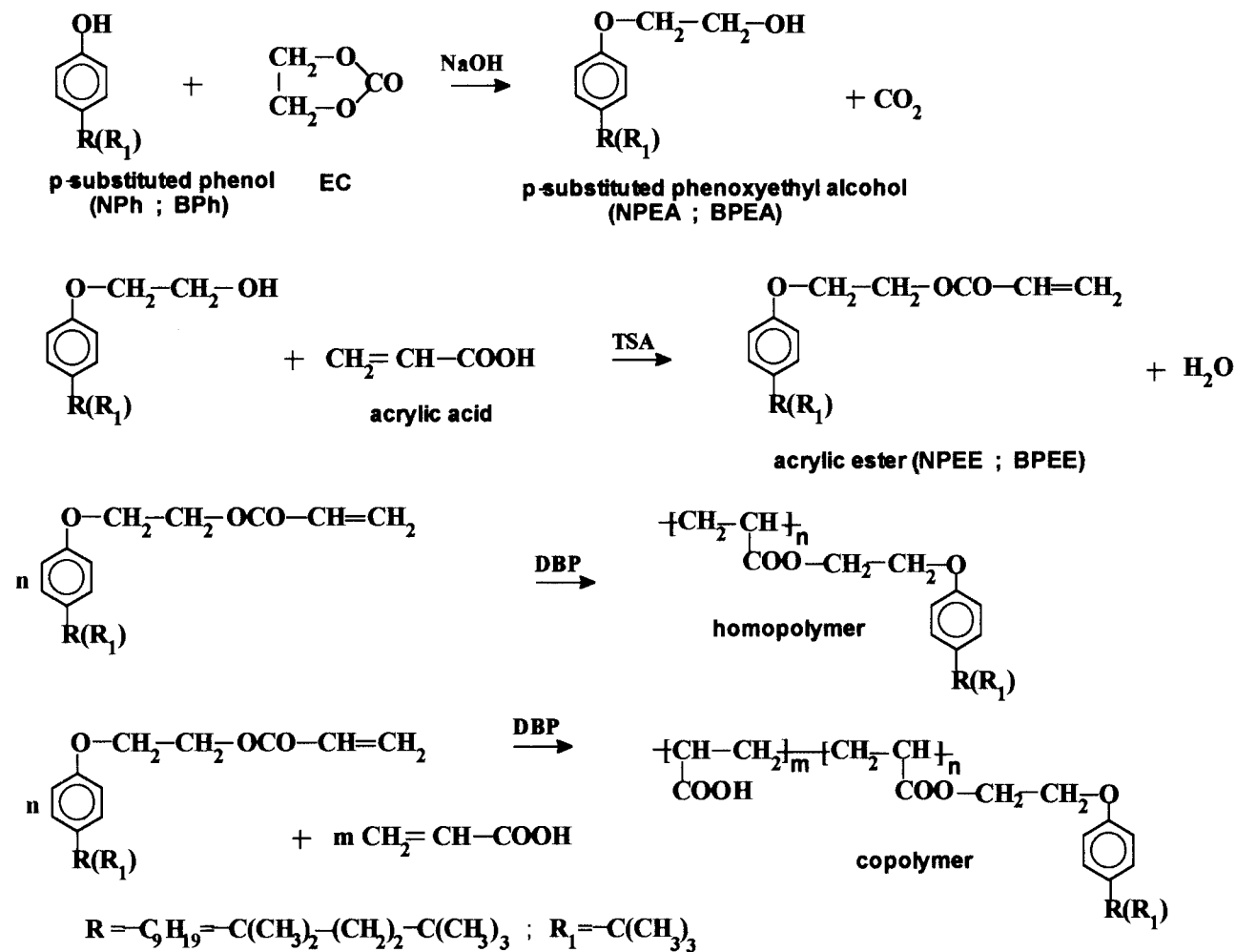
### Copolymerization of NPEE (BPEE) with AEHE and/or AA

The monomer mixtures consisting of (1) 90 wt % NPEE (BPEE) and 10 wt % AA; (2) 90 wt % AEHE and 10 wt % AA; and (3) 45 wt % of NPEE (BPEE), 45 wt % of AEHE, and 10 wt % of AA were performed. A total monomer amount of 72 g was used. To these mixtures, 28 g of solvent (cyclohexane) and 0.11 g (0.15 wt % addition) of DBP were added. The resulting monomer solutions were processed by the procedure used for the polymerization of NPEE or BPEE.

### Obtaining of the Adhesive Tapes

The concentrated polymer solutions were diluted with acetone to the 25 wt % concentration. The resulting solutions were applied, with a conventional draw bar procedure, on polyethylene glycol terephthalate backing films (40  $\mu\text{m}$  thick) in the required amounts to achieve a final dry coating weight of 35  $\text{g}/\text{m}^2$ . The drying of the wet adhesive





Scheme 1

films was performed by heating at 50°C for 15 min. The resulting adhesive films were cut into adhesive tapes 2.0 or 2.5 cm wide for testing.

## RESULTS AND DISCUSSION

### Monomer Synthesis

Two ester-type monomers (NPEE and BPEE) with aryl-alkyl groups in the structure were synthesized by condensation of the hydroxyethylated derivatives of NPh or BPh (NPEA and BPEA, respectively) with AA (Scheme 1).

By hydroxyethylation, the diminution of the acid character of phenolic OH was pursued. The modification of the phenols was carried out with EC and alkaline catalysts.<sup>55,56</sup> From the reaction, phenoxyethyl alcohols were obtained. These phe-

noxyethyl alcohols, unlike the starting phenols, could easily condense with AA by an elementary acid-catalyzed condensation reaction.

The hydroxyethylation reaction with EC presents some advantages in comparison with other similar routes, as follows:

- Ends in high transformation yields.
- Ensures the achievement of unitary (free of homologs) reaction products.
- Permits the obtainment of high-purity final products.

The transformation of the para-substituted phenols into the phenoxyethyl alcohols was shown by both the IR and <sup>1</sup>H-NMR spectral analysis data (Figs. 1 and 2) and the physicochemical characterization data of the reaction products

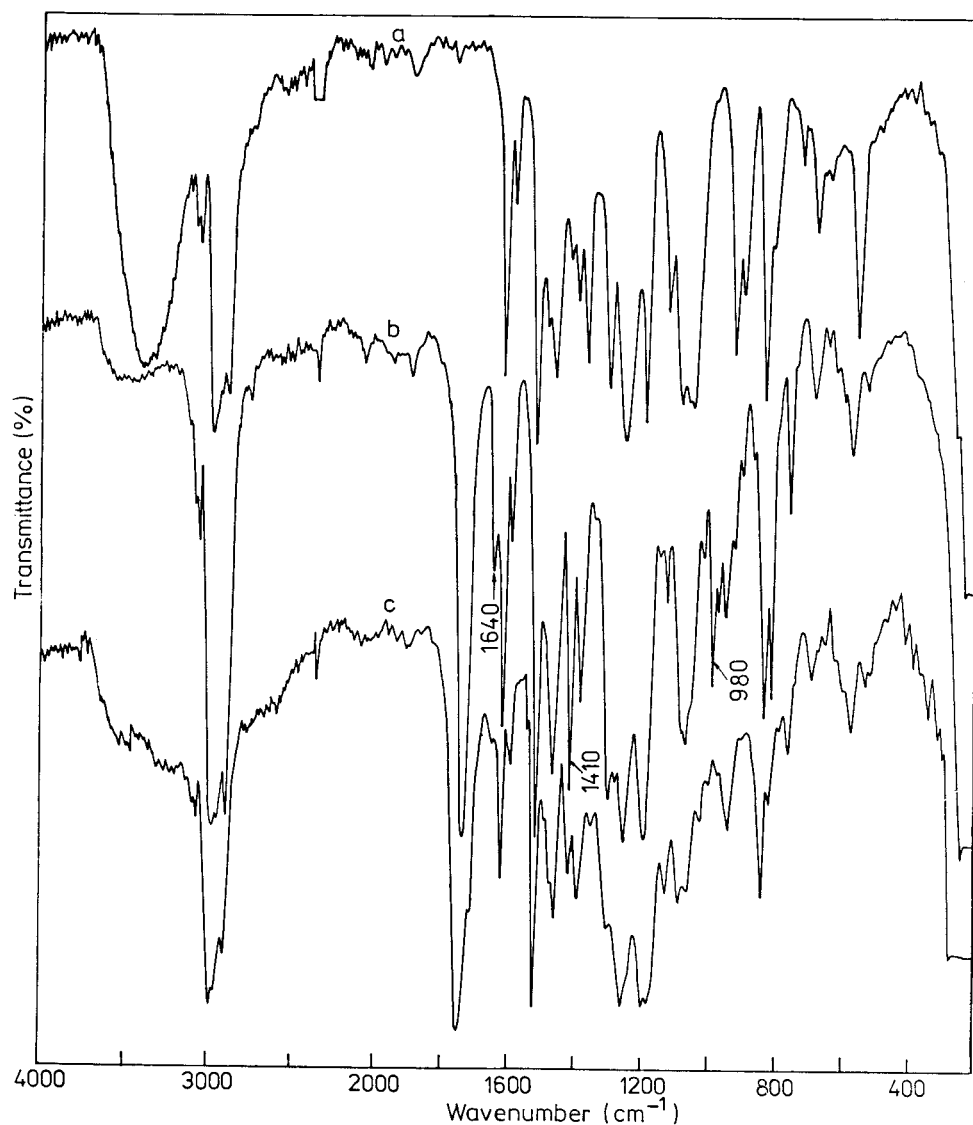


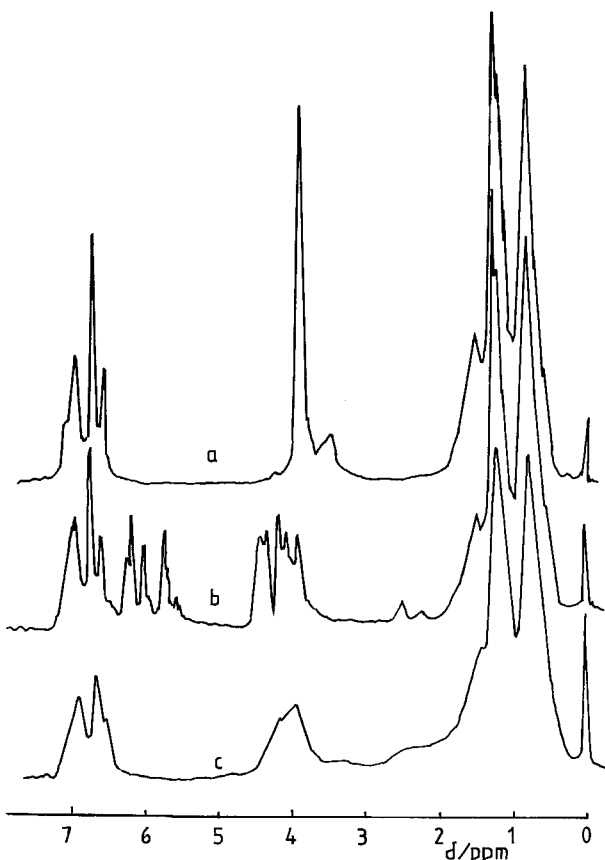
Figure 1 IR spectra of (a) NPEA, (b) NPEE, and (c) poly(NPEE).

(Table I). Thus, in the IR spectrum of NPEA [Fig. 1(a)], for instance, the formation of a phenoxyethyl alcohol was reflected by the existence of the absorption bands situated at  $1255\text{ cm}^{-1}$  ( $\nu_{\text{C}-\text{O}}$  in  $\text{C}_{\text{arom}}-\text{O}-\text{C}$ ) and  $1125\text{ cm}^{-1}$  ( $\nu_{\text{C}-\text{O}}$  in  $\text{C}_{\text{aliph}}-\text{O}-\text{C}$ ), characteristic of the newly formed etheric linkages, and at  $3350\text{ cm}^{-1}$  ( $\nu_{\text{OH}}$ ),  $1425\text{ cm}^{-1}$  ( $\delta_{\text{OH}}$ ),  $1045\text{ cm}^{-1}$  ( $\nu_{\text{C}-\text{OH}}$ ), and  $900$  and  $930\text{ cm}^{-1}$  ( $\gamma_{\text{OH}}$ ), characteristic of an aliphatic OH group. In the  $^1\text{H-NMR}$  spectrum [Fig. 2(a)], the chemical transformation was confirmed by the shifting of the peak at  $5.20\text{ ppm}$ , characteristic of phenolic OH, to the higher values of the field ( $3.95\text{ ppm}$ ), characteristic of alcoholic OH.

The synthesized phenoxyethyl alcohols were colorless substances, liquid at room temperature,

for which the main physicochemical characterization data are presented in Table I. One can observe that BPEA solidified at a somewhat higher than  $0^\circ\text{C}$  ( $+4.5^\circ\text{C}$ ), whereas NPEA froze at  $-41.5^\circ\text{C}$ . The products also had high purity.

When acrylic esters were synthesized, a great excess of AA was used (about 20 wt %) to ensure the complete consumption of the phenoxyethyl alcohols. If this excess was not used, during the purification of the reaction mass by washing with distilled water, these water-insoluble alcohols would accumulate in the upper liquid organic phase and eventually would accompany the desired reaction products. The subsequent separation of these compounds would be very difficult because of their very near physical



**Figure 2**  $^1\text{H-NMR}$  spectra of (a) NPEA, (b) NPEE, and (c) poly(NPEE).

properties, particularly the densities and the BPs.

Experimentally, it was observed that the presence of these phenoxyethyl alcohols, even in small quantities, in the mass of acrylic esters interfered with the polymerization. This was the first reason for which their complete removal was pursued. An another such reason was the fact that the presence of the phenoxyethyl alcohols in the polymer mass diminished their adhesive properties, acting as real plasticizers or as releasers. The OH content data of merely 0.1–0.15% and the AN data registered in the Table I prove the high purity of the synthesized acrylic esters.

As already mentioned, the final purification of the acrylic esters was performed by vacuum distillation at a reduced working rate. Higher distillation yields could have been achieved if hydroquinone used as polymerization inhibitor had not been entrained by the ester vapors leaving the boiling mass. Indeed, it was ascertained that as the distillation advanced and the boiling temperature exceeded the value of  $250^\circ\text{C}$ , the entrained

hydroquinone crystallized at the first contact with the cooled surface of the condenser. Afterward, as time went on, the crystallized hydroquinone again dissolved in the condensed ester and together collected in the distillation receiver. For this reason, toward the end, the monomer distillation practically developed in absence of the polymerization inhibitor. As a result, a part of the remaining crude product thermally polymerized, and the monomer extraction ceased early. The same phenomenon was also encountered when other specific polymerization inhibitors, such as 4-*tert*-butyl catechol, were used.

The data of spectral analysis confirmed the fact that the synthesized products were esters of phenoxyethyl alcohols with AA and still of high purity. Thus, in the IR spectrum of NPEE [Fig. 1(b)], for example, there were both the absorption bands characteristic of the newly formed ester linkages at  $1730\text{ cm}^{-1}$  ( $\nu_{\text{C=O}}$ ) and  $1060\text{ cm}^{-1}$  ( $\nu_{\text{C-O}}$  in esters) and the bands characteristic of acrylic unsaturation at  $1645\text{ cm}^{-1}$  ( $\nu_{\text{C=C}}$ ),  $1410\text{ cm}^{-1}$  ( $\delta_{\text{CH}}$  in acrylics), and  $980\text{ cm}^{-1}$  ( $\gamma_{\text{CH}}$  in acrylics). The absence from the spectrum of the absorption bands characteristic of the aliphatic OH group at  $3350\text{ cm}^{-1}$  ( $\nu_{\text{OH}}$ ),  $1425\text{ cm}^{-1}$  ( $\delta_{\text{OH}}$ ),  $1045\text{ cm}^{-1}$  ( $\nu_{\text{C-OH}}$ ), and  $900$  and  $930\text{ cm}^{-1}$  ( $\gamma_{\text{OH}}$ ) showed, on the one hand, that the esterification took place and, on the other hand, that the ester was a pure product.

In the  $^1\text{H-NMR}$  spectrum of the same NPEE [Fig. 2(b)], the nonyl group bonded to benzene ring resonated as a complex pattern of absorbance bands in the range from 0.82 to 1.89 ppm. The terminal methyl group appeared as a multiplet centered at 0.95 ppm, and the eight adjacent methylene groups formed an other multiplet centered at about 1.45 ppm. The methylene groups of the ethylene glycol moiety appeared as two multiplets centered at 4.05 and 4.45 ppm. The former represented the  $\text{CH}_2$  groups bonded to the ether oxygen, whereas the later arose from  $\text{CH}_2$  groups bonded to the ester oxygen atoms. The three olefinic protons formed a complex high-order pattern in the range from 5.6 to 6.4 ppm. The aromatic protons resonated in the range from 6.40 to 7.25 ppm. The hydrogens ortho to the OH group of the initial phenol resonated as a triplet centered at 6.70 ppm, and those ortho to the nonyl group appeared as a distorted multiplet centered at 7.05 ppm.

The  $^1\text{H-NMR}$  spectrum of BPEE was like of that of NPEE. Only the protons from the aliphatic rest bonded to the benzene ring resonated differ-

**Table I** Characterization Data of BPEA, NPEA, BPEE, and NPEE

Characteristic	BPEA	NPEA	BPEE	NPEE
State	Liquid	Liquid	Liquid	Liquid
Conversion (%) <sup>a</sup>	62.8	64.0	64.0	65.1
Density (g/cm <sup>3</sup> )	1.013	0.973	1.028	0.986
AN (mg of KOH/g)	0.0	0.20	1.45	1.0
HC (%)	8.57 (8.76) <sup>b</sup>	6.27 (6.44)	0.17 —	0.115 —
IN (g of I <sub>2</sub> /100 g)	—	—	100.72 (102.42)	78.38 (79.87)
Elemental analysis: C (%)	73.95 (74.23)	77.10 (77.27)	72.27 (72.58)	75.57 (75.47)
Elemental analysis: H (%)	9.03 (9.28)	10.29 (10.61)	8.18 (8.06)	9.26 (9.43)
Dynamic viscosity (mPa s)	192.7	683.0	36.8	119.8
BP (°C)	186 <sup>c</sup>	222 <sup>c</sup>	205 <sup>c</sup>	222 <sup>d</sup>
Melting point (°C)	4.5	-41.5	-17.5	-63.7
Color	Colorless	Colorless	Colorless	Colorless
Purity (%)	97.75 <sup>e</sup>	97.43 <sup>e</sup>	98.3 <sup>f</sup>	98.13 <sup>f</sup>

<sup>a</sup> Percent conversions determined from the weight of purified products referred to the weight of the reactants.

<sup>b</sup> Calculated values in parentheses.

<sup>c</sup> Measured at 40 hPa.

<sup>d</sup> Measured at 13.3 hPa.

<sup>e</sup> Determined from HC calculated/HC found.

<sup>f</sup> Determined from IN calculated/IN found.

ently. In the case of BPEE, the *tert*-butyl group resonated as a sharp singlet at 1.30 ppm.

The comparative examination of <sup>1</sup>H-NMR spectra of acrylic esters and of their corresponding phenoxyethyl alcohols, as well as the IR spectra, showed some important changes generated by the esterification of the OH groups, as follows:

- The modification of the structure of the peak representing the methylene groups from the hydroxyethyl rest, so that the initial singlet from the spectra of phenoxyethyl alcohols divided into two multiplets because of methylene groups bonded to etheric oxygen and ester oxygen, respectively.
- The appearance in the spectra of the peaks characteristic of the acrylic unsaturation at once with the disappearance of the peaks characteristic of the protons from the alcoholic OH groups.

The acrylic esters of phenoxyethyl alcohols were liquid at room temperature, colorless, and medium-viscous products and proper to all acrylic esters in odor. Some of their physicochemical characterization data are presented in Table I. An analysis of these data show that BPEE solidified

at -17.5°C. This means that the polymers resulting from its polymerization were not quite suitable for the preparation of self-adhesive materials because of their relative mechanical rigidity at normal temperature conditions. Contrariwise, NPEE, which presented a far lower solidification point, seemed to be better for such purposes.

The phenoxyethyl acrylates were stabilized with 0.1 wt % hydroquinone.

### Polymer Synthesis

Some specifications are noted here in connection with the NPEE (BPEE) polymerization procedure. Although the monomers were liquid materials, the polymerization in solution (cyclohexane, benzene) at high concentrations (70–72 wt %) was preferred. We chose this route with the intention of obtaining polymers with MWs as high as possible. The presence of the solvent in the reaction mass ensured, on the one hand, an effective removal of the reaction heat during the exothermal phase of the polymerization process and, on the other hand, an efficient stirring even in the last synthesis phases.

The reaction was initiated by means of free radicals (DBP). To facilitate the polymerization,



the inhibitor was removed from the monomers by washing with aqueous 5% NaOH.

Polymerization tests carried out by thermal initiation also ended in good results, but the reaction started at very high temperatures (over 240°C) and developed with rather low rates. The resulting polymers had lower MWs in comparison with those obtained by solution polymerization. Otherwise, as already mentioned, a such thermally initiated polymerization took place in the last part of the monomer purification. At that time, it was considered to be an undesirable process.

Therefore, NPPE and BPPE can be considered acrylic monomers with enough high chemical reactivity, despite their relatively complicated chemical structure. However, their reactivity was somewhat smaller compared to that of other acrylates. As proofs in favor of this assertion serve, the relatively blurred exothermal effect (2–5°C) registered at the homopolymerization or the higher reaction duration required for their complete polymerization.

The obtained polymer solutions were used as obtained from synthesis when adhesive properties were tested. For all the other analyses, only the polymers precipitated into methanol were used.

The chemical structures proposed for the products obtained from the homopolymerization of NPPE or BPPE are shown in Scheme 1. The spectral analysis data confirmed this structure. The IR and <sup>1</sup>H-NMR spectra of poly(NPPE) are shown in Figures 1(c) and 2(c), respectively. Its IR spectrum did not differ too much from that of the corresponding monomer [Fig. 1(b)]. Only the bands characteristic of the double bonds, at 1640 cm<sup>-1</sup> ( $\nu_{C=C}$ ), 1410 cm<sup>-1</sup> ( $\delta_{CH}$ ), and 980 cm<sup>-1</sup> ( $\gamma_{CH}$ ), disappeared as a consequence of their consumption in the polymerization reaction. In the <sup>1</sup>H-NMR spectrum of poly(NPPE), the disappearance of the peaks characteristic of the acrylic unsaturation, at 5.60–6.40 ppm, were also observed.

### Adhesive Properties

NPPE and BPPE homopolymers were liquid, highly viscous, sticky products of light yellow color. They were soluble in benzene, toluene, ethyl acetate, 1,2 dichloroethane, trichloromethane, methyl ethyl ketone, N,N' dimethylformamid, and acetone and insoluble in aliphatic alcohols (methyl, ethyl, isopropyl) or petroleum ether (BP 30–60°C). As the viscosity data from Table II

prove, they were high-MW polymers that also presented excellent adhesive properties.

As a rule, adhesion, the ability of self-adhesive substances to stick strongly to the surfaces in contact, is measured by the most commonly accepted test, namely the 180°-angle peel test. However, peel adhesion does not constitute a particularly good measure of the multitude of performances of the adhesives. Sometimes, when no peel is required, it can become even useless. From these reasons and with the intention of achieving a better characterization of the synthesized adhesives, we also used the 0°-angle hold test. In this context, the 180°-angle peel test measures a combination of adhesion and cohesion properties, whereas the 0°-angle hold test measures the internal strength.

The experimental program, consisting of 10 experiments (in fact, 10 polymer or copolymer formulae on the basis of NPPE, BPPE, AEHE, and AA presented in Table II), was conceived and performed to obtain as complete as possible information about the adhesive properties of poly(NPPE) and poly(BPPE). We obtained some adhesive tapes by applying the polymer solutions onto the polyethylene terephthalate backing films. Table II includes the data acquired by the testing of these adhesive tapes in accordance with the 0°-angle hold test and the 180°-angle peel test. The polymers obtained from Experiments 1 and 4 represent reference adhesive materials (controls), the first for NPPE and BPPE homopolymers (Experiments 2 and 3) and the second for the copolymers with AA and/or AEHE in composition (Experiments 5–10).

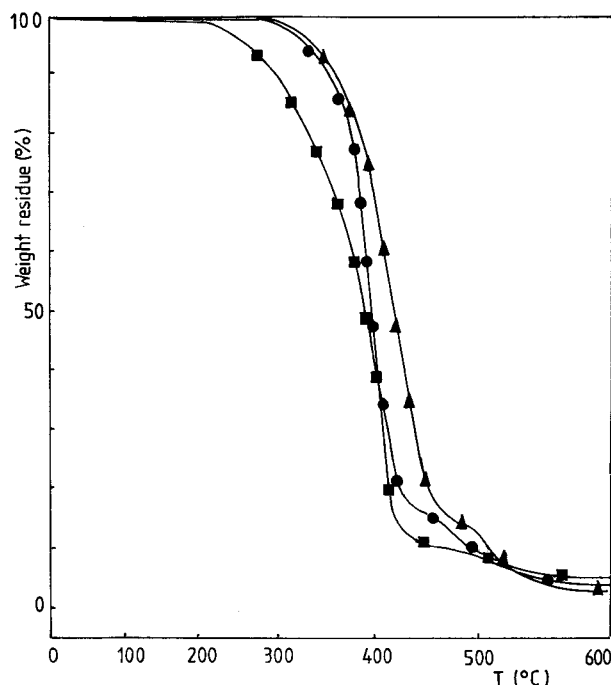
The data corresponding to Experiments 1–3 show that poly(NPPE) and poly(BPPE) exhibited adhesive and cohesive properties far higher than those presented by the control [poly(AEHE), Experiment 1]. These homopolymers can be used as pressure-sensitive adhesives, unlike the control, which acquired somewhat significant values for the two tests only after the copolymerization with AA (Experiment 4, control in this turn) or other comonomers as, for example, NPPE or BPPE themselves (Experiments 7 and 8). An examination of the data listed in the Table II also reveals that the polymers containing BPPE presented greater cohesive strengths (0°-angle hold test data) compared with the polymers containing NPPE. This could be ascribed to the higher solidification point (–17,5°C) of BPPE.

The copolymerization abilities of NPPE and BPPE were tested by copolymerization with AA

**Table II** Experimental Program and Some Characterization Data for the Homopolymers and Copolymers of NPPE, BPPE, AEHE, and AA

Experiment Number	Polymer	Copolymer Ratio (w/w)	Conversion (%)	Color	Viscosity			Adhesion Properties	
					Dynamic <sup>b</sup> (mPa s)	Inherent <sup>c</sup> (mL/g)	0°-Angle Hold Test (min)	180°-Angle Peel Test (cN/cm)	
1	Poly(AEHE) <sup>a</sup>	100	99.0	Colorless	46.0	14.53	0.15	30 <sup>d</sup>	
2	Poly(BPPE)	100	99.0	Yellow	520.0	47.16	110	405 <sup>e</sup>	
3	Poly(NPPE)	100	97.8	Yellow	813.8	64.30	18	590 <sup>e</sup>	
4	Poly(AEHE/AA) <sup>a</sup>	90/10	99.1	Colorless	312.0	—	2.5	940 <sup>d</sup>	
5	Poly(BPPE/AA)	90/10	93.7	Yellow	403.7	—	1460	735 <sup>e</sup>	
6	Poly(NPPE/AA)	90/10	96.2	Yellow	977.0	—	835	960 <sup>f</sup>	
7	Poly(BPPE/AEHE)	50/50	94.2	Yellow	105.3	—	0.55	70 <sup>d</sup>	
8	Poly(NPPE/AEHE)	50/50	99.0	Yellow	250.7	—	0.87	82 <sup>d</sup>	
9	Poly(BPPE/AEHE/AA)	45/45/10	97.3	Yellow	782.0	—	305	480 <sup>e</sup>	
10	Poly(NPPE/AEHE/AA)	45/45/10	94.5	Yellow	919.7	—	184	550 <sup>e</sup>	

<sup>a</sup> Control.<sup>b</sup> Determined on the 50% solutions in acetone at 25°C.<sup>c</sup> Measured with 0.5% (w/v) solutions in acetone at 25°C.<sup>d</sup> Peeling associated with the splitting of the adhesive layer between the steel plate and the backing film.<sup>e</sup> Flawless release of the adhesive tape from the steel plate.<sup>f</sup> The adhesive was transferred to the plate.



**Figure 3** TGA curves of (■) poly(AEHE), (▲) poly(NPEE), and (●) poly(BPEE).

(Experiments 5 and 6) or with AEHE (Experiments 7 and 8). In the first case, a copolymerization ratio of 90:10 (w/w) was used, whereas in the second, a ratio of 50:50 (w/w) was used. Both NPEE and BPEE displayed high capacities to copolymerize with other monomers frequently used in the synthesis of adhesive materials. The data included in Table II show that the copolymers acquired in presence of AA presented better results in comparison with both the control (Experiment 4) and the AEHE copolymers (Experiments 7 and 8). This observation immediately and implicitly led to the idea of the achievement of ternary copolymers on the basis of NPEE (BPEE), AEHE, and AA (Experiments 9 and 10). These copolymers behaved well as pressure-sensitive adhesives and presented the best values for adhesiveness and cohesiveness, so that at least in the conditions of these studies, they represented the optimum formulae for the achievement of the best adhesives based on the phenoxyethyl acrylates.

### Thermal Properties

The thermal behavior of the polymers was evaluated by TGA. Figure 3 shows the thermograms of poly(NPEE) and poly(BPEE), and Table III sum-

marizes some thermal characterization data calculated from TGA curves. For comparative purposes, the data regarding the thermal behavior of poly(AEHE), synthesized in the same reaction conditions, are also included in Figure 3 and Table III.

As the results from Figure 3 show, the initial weight loss was registered at 285°C for poly(NPEE), at 280°C for poly(BPEE), and at only 185°C for poly(AEHE). The rate of the decomposition process appeared to be very fast between 315 and 475°C for poly(NPEE), between 320 and 420°C for poly(BPEE), and between 245 and 420°C for poly(AEHE). There was very good agreement with the literature data, which specify that the upper limit of the working temperature of the acrylic polymers usually used as adhesives is 235°C,<sup>1</sup> and the value of the temperature at which the process of thermal decomposition of poly(AEHE) became very fast was 245°C.

Examination of the data listed in the Table III reveals that the initial decomposition temperature ( $DT_0$ ) or the decomposition temperature at 10% weight loss ( $DT_{10}$ ) values of poly(AEHE) were by far lower than those of the polymers containing aromatic nuclei in the structure. When  $DT_0$  is considered as a criterion of thermostability, it follows that poly(NPEE) and poly(BPEE) presented thermostabilities with 90–100°C higher in comparison to poly(AEHE). When poly(NPEE) and poly(BPEE) were compared, although the two polymers presented similar thermal behaviors, it was found that poly(NPEE) exhibited a slightly higher thermal stability.

Therefore, the introduction of an aryl component into the acrylic ester structure led to an increase in thermostability. This finding can be ascribed to the smaller vulnerability toward the thermooxidative processes of the aromatic-aliphatic rests from poly(NPEE) or poly(BPEE) in comparison with the aliphatic rests from poly(AEHE).

**Table III** Thermal Properties of Synthesized Polymers

Polymer	$DT_0$ (°C)	$DT_{10}$ (°C)	WL500 (%)
Poly(AEHE)	185	265	92
Poly(NPEE)	285	360	86
Poly(BPEE)	280	355	89

WL500 = weight loss at 500°C.

## CONCLUSIONS

Two new acrylic esters containing aromatic-aliphatic groups in structure were synthesized and characterized. These acrylates were synthesized by condensation of AA with the phenoxyethyl alcohols obtained from the hydroxyethylation reaction between 1,3-dioxolan-2-ona and NPh or BPh. The monomers were polymerized in solution by a free-radical-initiated reaction. Their chemical reactivity was high enough to ensure the achievement of high-MW polymers. These polymers presented both good adhesion and cohesion characteristics and thermostabilities far higher than those of ordinary polyacrylates. They were suitable for special purposes, for example, preparation of adhesive compositions and/or adhesive tapes that must act at elevated temperatures.

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