

Synthesis, Polymerization, and End-Use Evaluation of 3-Pentadecylphenyl Acrylate and Methacrylate

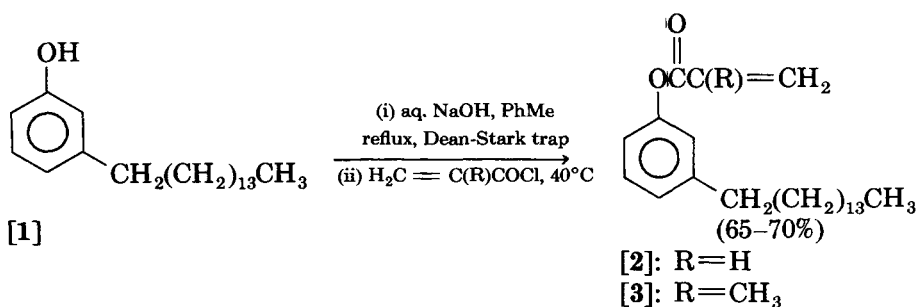
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Synopsis

Two new polymerizable monomers, namely, 3-pentadecylphenyl acrylate and methacrylate, were synthesized starting from Cashew Nut Shell Liquid. The synthetic method used is simple, and is of general utility. These monomers were homopolymerized by bulk, solution, and emulsion polymerization techniques which yielded moderately high molecular weight polymers that showed promise as pressure-sensitive adhesive.

INTRODUCTION

Cashew Nut Shell Liquid (8007-24-7), a vesicant oily liquid obtained during the isolation of cashew kernels by heat treatment, has given rise to a number of products of commercial importance. For example, resins derived from CNSL and its derivatives have shown considerable promise as media for surface coatings, friction-resistance components, laminates, moulding materials, rubber-compounding ingredients, ion-exchange membranes, and adhesives.¹ Cardanol (37330-39-5), the major component (> 95%) of the double-distilled CNSL,² can be conveniently hydrogenated^{3,4} to obtain 3-pentadecylphenol [1] (501-24-6; H-03049), which has none of the vesicant action of the liquid. We report herein a simple and convenient method for the synthesis of two *new* polymerizable vinyl monomers, namely, 3-pentadecyl-phenyl acrylate and methacrylate [2] and [3] from [1]. *The method is of general utility.*



We further report the results of our study on the polymerization of the aforesaid monomers, and on the end-use evaluation of the polymers for use as pressure-sensitive adhesives.

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EXPERIMENTAL

Materials

3-Pentadecylphenol [1]

Double-distilled cardanol, which contained about 2–3% cardol (16737-82-9), was hydrogenated in a Parr medium pressure hydrogenator using the procedure of Madhusudhan et al.⁴ The hydrogenated product was freed from catalyst by filtration while hot, and the filtrate distilled under reduced pressure. The fraction collected between 198 and 200°C/1–2 mmHg was twice crystallized from *n*-hexane to give pure (> 99%, HPLC) 3-pentadecylphenol [1] (mp 50.5 to 51.0°C).

Acryloyl chloride (814-68-6) and methacryloyl chloride (920-46-7) were prepared by the procedure of Stempel et al.⁵

Monomer Synthesis

3-Pentadecylphenyl Acrylate [2]

First, 30.4 g (0.1 mol) of 3-pentadecylphenol [1] in 250 mL of dry toluene was taken in a 1-L, three-neck flask equipped with an efficient stirrer, a dropping funnel, and a Dean-Stark trap. A concentrated aqueous solution of sodium hydroxide (4.4 g, 0.11 mol in 5 mL H₂O) was slowly added into it while the solution was vigorously stirred and heated to reflux. Refluxing continued until azeotropic removal of water was complete (ca. 6.8 mL, 3–4 h). The contents of the flask were cooled to 40°C and hydroquinone (1% on the weight of [1]) was added to it. Later, freshly distilled acryloyl chloride⁵ (10.86 g, 0.12 mol) was added dropwise into the stirred solution with the exclusion of moisture. The stirring was continued until micro-thin layer chromatography indicated attainment of maximum conversion (3–4 h). The contents of the flask were filtered to remove the sodium chloride formed. Filtrate was freed from toluene under reduced pressure. The crude product, thus obtained, was distilled under highly reduced pressure (< 0.01 mmHg) over 0.1% copper rosinate followed by adsorption through silica gel, using *n*-hexane as eluting solvent to provide pure (> 99% HPLC) 3-pentadecylphenyl acrylate [2] in 65–70% yield (n_D^{25} 1.4824).

IR (cm⁻¹): (liq.) 3040 (vinyl unsaturation), 1750 (ester), 1290 (vinyl), 1025, 980, 965 and 740 (acrylic ester)

¹HNMR (δ): (CDCl₃) 0.8 (t, 3H, CH₃), 1.11 (m, 26H, —(CH₂)—₁₃), 2.2–2.6 (t, 2H, CH₂), 5.1–5.4 (m, 2H, =CH₂), 5.6–5.9 (m, H, —CH=), 6.1–6.6 (m, 4H, ring hydrogens)

Mass (*m/z*): (70 eV) 55 (100%), 304 [(M-55) + 1], 358 (M⁺)

3-Pentadecylphenyl Methacrylate [3]

The same procedure as that for [2] was followed using methacryloyl chloride⁵ (12.55 g, 0.12 mol), freshly distilled, in place of acryloyl chloride.

Distillation over copper rosinate followed by column chromatographic purification, as stated for [2], provided pure (> 99% HPLC) 3-pentadecylphenyl methacrylate in 65–70% yield (n_D^{25} 1.4869).

IR (cm^{-1}): (liq.) 3040 (vinyl unsaturation), 1740 (ester), 1290 (vinyl), 1320 and 940 (methacrylic ester)

$^1\text{HNMR}$ (δ): (CDCl_3) 0.8 (t, 3H, CH_3), 1.1 (m, 26H, $-(\text{CH}_2)_{13}$) 1.84 (s, 3H, CH_3), 2.1–2.4 (t, 2H, CH_2), 5.1 and 5.6 (s, s, 2H= CH_2), 6.1–6.6 (m, 4H, ring hydrogens)

Mass (m/z): 69 (100%), 372 (M^+).

Polymerization

Solution Polymerization

Monomer and dry benzene in the ratio of 1:2 (w/v) together with the required quantity of benzoyl peroxide initiator was weighed into a tube (having a constriction near its open end so as to enable rapid sealing of the tube) which was purged thoroughly with nitrogen. Pure nitrogen was gently introduced into the tube to provide a blanket. Later, the tube was cooled by immersion in a dry ice-acetone bath, evacuated (1–2 mmHg), and the tube was sealed at the constriction. Finally, the polymerization tube was placed in a water thermostat maintained at $70 \pm 0.1^\circ\text{C}$ for the required period. At the end of the reaction period, the tube was cooled to room temperature, neatly cut open slightly below the constriction (so that the polymer could be dissolved in benzene, which was usually necessary to facilitate flow), and the contents poured into a large excess of methanol under constant stirring with a glass rod. The precipitated polymer was transferred into a weighed flask, freed from solvent under vacuum, and weighed. Percent conversion was calculated from the weight of the precipitated polymer.

Maximum conversion (ca. 95%) was obtained when 2 mol% of peroxide was used as the initiator and the polymerization was carried out for 32–36 h. The intrinsic viscosities and the number-average molecular weights (Damfdruck-Osmometer) of the polymers are given in Table I.

TABLE I
Intrinsic Viscosities and Molecular Weights (\bar{M}_n) of 3-Pentadecylphenyl Acrylate and Methacrylate Prepared by Different Polymerization Techniques

Monomer	Technique of polymerization	$[\eta]^{30}$ benzene	\bar{M}_n
3-Pentadecylphenyl acrylate	Bulk	0.51	14,000–15,000
	Solution	0.54	16,000–17,000
	Emulsion	0.58	19,000–21,000
3-Pentadecylphenyl metacrylate	Bulk	0.52	14,000–15,000
	Solution	0.56	17,000–18,000
	Emulsion	0.59	20,000–21,000

Bulk Polymerization

Essentially the same procedure as above was followed for the bulk polymerization of the two monomers under study, excepting that no solvent was used and that cooling of the polymerization tube at subzero temperature was not necessary. The intrinsic viscosities and the number-average molecular weights of the polymers are given in Table I.

Emulsion Polymerization

Emulsion polymerization of 3-pentadecylphenyl acrylate and methacrylate were carried out using the standard procedure of Fisher and Mast⁶ suitably modified to meet our requirements as described earlier.⁷ The intrinsic viscosities and the number-average molecular weights of the polymers are given in Table I.

End-Use Evaluation

The polymers, obtained by emulsion polymerization technique, were evaluated for their use as pressure-sensitive adhesive. A number of porous and nonporous surfaces were used for the study. The surfaces were initially degreased by cleaning with trichloroethylene and were then uniformly coated with the material by using a film applicator. The relative peel resistance of the adhesive bond between two flexible adherends was determined by 180° peel test as per ASTM D-903 method. The adhesive stripping strength of a flexible member of an assembly bonded with adhesive to another rigid member (chip board) was also determined by 180° peel test as per ASTM D-903 (Table II).

The tests were performed on a standard tensile testing machine INSTRON Universal testing instrument (Table Model 1026), and readings are reported directly as grams per linear inch (gli). The gauge-stripping length of 15 cm and a chart speed of 10 cm/min were employed in all cases.

Based on the observations recorded in Table II, for poly(3-pentadecylphenyl acrylate), it can be deduced that the said polymer is promising as a pressure-sensitive adhesive for bonding (i) PVC tapes to paper, laminated sheet, glass, and mild steel, (ii) aluminum tapes to aluminum, cellophane, paper, laminated sheet, mild steel, and chip board, (iii) cellophane tapes to

TABLE II
180° Peel Strength (gli) of Poly(3-Pentadecylphenyl Acrylate) between Different Adherends

Adherends	PVC	Aluminum	Cellophane	Paper	Rexin
PVC	85	55	70	440	44
Aluminum	55	380	250	550	88
Cellophane	70	250	120	280	30
Paper	440	550	280	400	450
Rexin	44	88	30	450	100
Laminated sheet	700	800	250	500	88
Mild steel	280	715	280	1400	70
Glass	440	160	440	1100	20
Chip board	175	700	600	830	40

aluminum, paper, laminated sheet, mild steel, and chip board, and (iv) paper tapes to all the surfaces studied.

The poly(3-pentadecylphenyl methacrylate), when subjected to the aforesaid test, provided more or less similar data.

CONCLUSION

The polymers of 3-pentadecylphenyl acrylate and methacrylate, conveniently synthesizable from the agro bye-product Cashew Nut Shell Liquid, have shown promise as a pressure-sensitive adhesive.

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Received November 11, 1987

Accepted December 16, 1987