Polymerizable Monomers From Castor Oil: II. Syntheses of Some Divinyl Monomers

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Abstract

Ten divinyl monomers have been synthesized, based on commonly available products derived from castor oil, in 50–100 g lots of high purity. These were characterized by infrared spectroscopy and their purity was checked by chromatographic methods. Boiling points, refractive indices and iodine values of the products are reported. Thin layer chromatography of divinyl monomers based on decanedioic acid has also been studied.

Introduction

Polymerization studies on long chain vinyl monomers derived from oils and fats have received considerable attention in recent years because of their significant theoretical and practical importance (1). We have earlier reported (2) preparation of a wide range of vinyl monomers based on undecenoic acid, a pyrolysis product of castor oil, and several of its derivatives. We now report the syntheses of some divinyl monomers derived from commonly available products based on castor oil, i.e., sebacic acid, 10-undecenoic acid and 12-hydroxystearic acid. Some 50 g each of the purified samples of the monomers were sent to the U.S. Department of Agriculture, Western Utilization Research and Development Division, Albany, California, for their evaluation as comonomers in crosslinking speciality plastics and resins and for studies in crosslinking of cotton cellulose.

Also, we have suitably modified the process involving reaction between acrylyl chloride and hydroxyl group to prepare, in good yields, the acrylic and methacrylic esters of 1,12-octadecanediol. One of the hydroxyl groups is secondary therefore Rehberg's procedure (3) probably did not work. This is in agreement with similar observations reported by Nelson and Applewhite (4). They worked out a two-step process involving the use of β-chloropropionyl chloride which gave the secondary acrylate in about 90% yield. They also tried the reaction between a secondary hydroxyl group and acrylyl chloride but the yields were not satisfactory. From Hickmott's work (5) it appears that the lower yield in the latter process could probably be attributed to the formation of a water soluble complex between acrylyl chloride and the base. Thus, a considerable amount of tertiary amine which was meant to fix the hydrogen chloride liberated in the reaction was wasted, together with stoichiometric quantities of acrylyl chloride. The method of the modification suggested at present consists of adding alternately small portions of a chloroform solution of acrylyl chloride followed by the tertiary base in a quantity just sufficient to fix the liberated hydrogen chloride. This minimises the formation of water soluble complex between acrylyl chloride and the base.

Experimental Procedures

Materials

Pure sebacic acid (also known as decanedioic acid and octane 1:8 dicarboxylic acid) and 10-undecenoic acid were available commercially and were therefore used. Preparation of 11-allyloxyundecanoic acid has been reported in our earlier article (2).

1,10-Decanediol and mixed alcohols of castor fatty acids were obtained by sodium reduction of dimethyl sebacate and neutral castor oil by Hansley's procedure (6), however 8.4 and 5.4 g atoms of sodium and 4.2 and 2.1 moles of dry *sec*-butanol were used. While processing the reduction products of dimethyl sebacate, adequate care was taken to avoid the possible loss of 1,10-decanediol during washing etc., since the diol is fairly soluble in water. The crude alcohol was finally crystallized from acetone to give pure 1,10-decanediol, mp 71–72 C.

Hydrogenation over 1% of Raney nickel at 100 C and 150 psig of the mixed alcohols of castor fatty acids, followed by crystallizing the product twice from an excess of *n-hexane,* gave pure 1,12-octadecanediol, mp 77–77.5 C.

Acrylyl and methacrylyl chlorides were prepared by the procedure of Stempel et al. (7).

Preparative Methods

Allyl Esters. Diallyl sebacate was prepared by refluxing, 1 mole of sebacic acid and 10 moles of dry allyl alcohol for 6–8 hr using 2% *p*-toluenesulphonic acid as the catalyst. When the reaction was complete, sodium acetate, in a quantity sufficient to destroy the catalyst, was added to the reaction flask, excess allyl alcohol was recovered, and the crude ester was processed in the usual manner.

Allyl Ether. 1,10-Diallyloxydecane was prepared by reacting 1 mole of the disodioalkoxide of the diol with 2.5 to 3.5 moles of allyl bromide in the manner described in our earlier paper (2). The method, however, did not work well with 1,12-octadecanediol, probably because one of the hydroxyl groups is secondary.

Vinyl Esters. Both vinyl 11-allyloxyundecanoate and divinyl sebacate were prepared in high yields by refluxing 1 mole of the acid with 6 and 10 moles of stabilized vinyl acetate for 3 hr in the presence of catalytic amounts of mercuric acetate and 40% hydrofluoric acid (8).

Vinyl Ethers. Both 1,10-divinyloxydecane and 1,12-divinyloxyoctadecane were prepared in good yields by transetherification with ethyl vinyl ether in the presence of mercuric acetate (9). Use of *n*-butyl vinyl ether as transvinylating agent (10) did not prove to be of any advantage in either case.

Acrylic and Methacrylic Esters. Acrylic and methacrylic esters of 1,10-decanediol were prepared by Rheberg's procedure (3) involving alcoholysis of methyl acrylate or methyl methacrylate in the presence of an acidic catalyst, such as naphthalene 2-sulfonic acid, and a polymerization inhibitor such as hydroquinone, quinol, etc. However, the process did not work with 1,12-octadecanediol, therefore the reaction with acrylyl chloride was employed after the modifications which have been explained earlier. The details of the process are as follows:

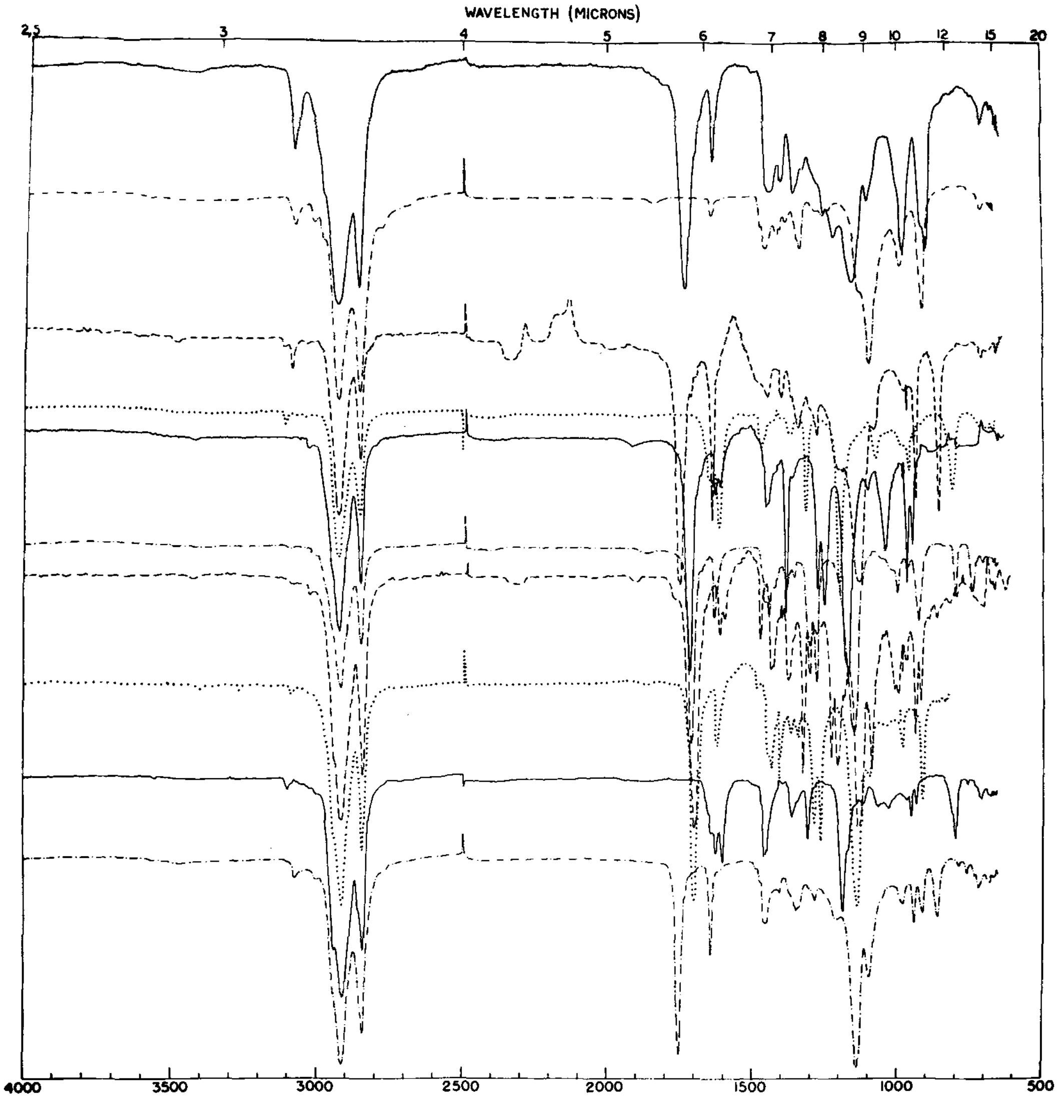

FIG. 1. Infrared spectra (from top to bottom) of diallyl sebacate, 1,10-diallyloxydecane, divinyl sebacate, 1,10-divinyloxydecane, 1,10-diacryloxydecane, 1,10-dimethacryloxydecane, 1,12-diacryloxyoctadecane, 1,12-dimethacryloxyoctadecane, 1,12-divinyloxyoctadecane and vinyl 11-allyloxyundecanoate.

A solution of 1,12-dihydroxyoctadecane (0.15 mole) in 200 ml of chloroform containing 2 g hydroquinone was taken in a 500 ml four neck flask equipped with a mechanical stirrer, two dropping funnels and a condenser with calcium chloride guard tube. The contents were heated to 60–62 C and stirred vigorously. A solution of acrylyl chloride (0.45 mole) in chloroform (50 ml) and triethylamine (0.45 mole) was added alternately and in small instalments. The course of the reaction was followed by using micro thin layer chromatography (TLC) plates. Finally the contents of the flask were diluted with petroleum ether in order to completely flush out the triethylamine hydrochloride which was filtered off. The filtrate was washed with dilute hydrochloric acid solution to remove any remaining triethylamine, then with 10% solution of potassium carbonate to remove the acrylic acid formed in the process, and then with distilled water until neutral. The solution was then dried over anhydrous sodium sulfate and the solvent stripped off.

1,12-Dimethacryloxyoctadecane was prepared in a

TABLE I
Physicochemical Characteristics of Some Divinyl Monomers Based on Castor Oil

Monomers	Boiling point (°C/mm Hg)	Refractive index (at °C)	Total iodine value[a]	
			Found	Calculated
Diallyl sebacate	178–80/2	1.4492 (39)	178.5	180.0
1,10-Diallyloxydecane	144/1–2	1.4441 (33)	197.8	200.0
Vinyl 11-allyloxyundecanoate	154/1–2	1.4512 (28)	187.2	189.6
Divinyl sebacate	166–68/1–2	1.4506 (30)	196.4	200.0
1,10-Divinyloxydecane	156–58/1–2	1.4482 (30)	b	
1,12-Divinyloxyoctadecane	200/1–2	1.4470 (30)	b	
1,10-Diacryloxydecane	180–81/1–2	1.4520 (33)	178.2	180.0
1,12-Diacryloxyoctadecane	168–70/0.02	1.4628 (28)	126.6	128.9
1,10-Dimethacryloxydecane	185–86/0.8	1.4560 (30)	162.8	163.9
1,12-Dimethacryloxyoctadecane	176–78/0.02	1.4592 (30)	118.1	120.4

[a] Determined by using pyridine sulfate dibromide as halogenating agent (11).
[b] Percentage vinyl ether, determined by iodometric method (12), ranged from 98 to 100.

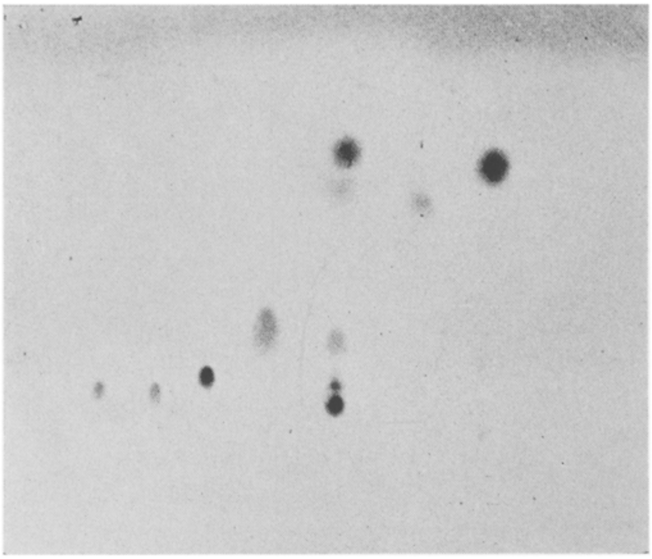

FIG. 2. Chromatogram showing the position of six divinyl monomers and a synthetic mixture of these on direct plate, the solvent system being *n-hexane-ether* (100:5 v/v); from left to right: diallyl sebacate, 1-10-diacryloxydecane, 1,10-dimethacryloxydecane, divinylsebacate, synthetic mixture, 1,10-diallyloxydecane and 1,10-divinyloxydecane.

similar manner from 1,12-octadecanediol using methacrylyl chloride in place of acrylyl chloride. In this process, formation of some hydroquinone diacrylate or dimethacrylate was also noted, however this could be removed during the distillation operation.

Purification and characterization. Each of the monomers was purified by one or two distillations under reduced pressure, over 0.1% copper rosinate, followed by adsorption through alumina or silica gel column. The products were characterized by infrared spectroscopy (Fig. 1) and the purity was checked by chromatographic methods. Some of the physicochemical characteristics of the monomers are listed in Table I.

Thin layer chromatography of the divinyl monomers based on sebacic acid. Figure 2 shows the positions of six divinyl monomers derived from sebacic acid and that of a synthetic mixture of these on a direct TLC plate coated with approximately 270 μ thickness of silica gel G and developed with *n*-hexane-ethyl ether (100:5 v/v). All but diallyl sebacate and 1,10-diacryloxydecane were resolved individually. The $R_f \times 100$ values for diallyl sebacate, 1,10-diacryloxydecane, 1,10-dimethacryloxydecane, divinyl sebacate, 1,10-diallyloxydecane and 1,10-divinyloxydecane were 6, 6, 10, 19, 46 and 54, respectively.

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