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SYNTHESIS AND PROPERTIES OF MALEIC ANHYDRIDE - CROTONIC ACID-VINYL ACETATE TERPOLYMER

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Free radical terpolymerization of maleic anhydride (in the form of halfester of maleic acid) crotonic acid and vinyl acetate has been accomplished at 75-80° using benzoyl peroxide as initiator. It has been observed that three monomers polymerise simultaneously and form terpolymer in all monomeric ratios. Terpolymers of 8394-18434 molecular weight are obtained. These are white solid substances soluble in most of organic solvents that softens at 70-90°. The refractive index of terpolymer samples ranges 1.3610–1.3635. The terpolymers may be used in the preparation of hair spray as the film forming agent.

Key words: Plasticizer, Adhesion, Film forming agent.

Introduction

The copolymers and terpolymers are familiar in the preparation of various types of cosmetics products like shampoos, nail varnishes, lotions, hair sprays, sun screen preparations. In our earlier paper [1] a terpolymer based on acrylates has been reported. It has commercial applications as plasticizer in nail varnishes and makes nail varnishes stable and produces thin films with excellent adhesion and good gloss to the nail keratin. Survey of the literature provides so many references describing the use of such polymers in hair sprays [2-5]. One of them is a copolymer of crotonic acid and vinyl acetate under the designation luvi set Ca66. It is an odourless copolymer containing carboxyl groups which is used as a film forming agent in both hair sprays and setting lotions. But there were some drawbacks in its use like inadequate clarity of films, gloss and undesirable flaking. To overcome these difficulties this copolymer was further improved by treating the binary mixture of vinyl monomers with monoalkyl maleate [4]. It proved a better film forming agent. Attempts have been made to improve the quality of the product by preparing it at different monomeric ratios. In this paper we report the synthesis of terpolymer of maleic anhydride (as halfester of maleic acid), crotonic acid and vinyl acetate in all monomeric ratios using benzoyl peroxide as initiator. Some physical parameters effective in improving the quality of the product are also studied.

Experimental

Maleic anhydride (Aldrich) crotonic acid 2-amino-2-methyl 1,3-propanediol (AMPD) of E. Merck were used without further purification. Vinyl acetate, ethyl alcohol, acetone, ethyl acetate etc. were distilled before use. Benzoyl peroxide, AR grade was recrystallised twice in chloroform.

Procedure of polymerization. Polymerization was carried out in a flange flask fitted with condenser, separating funnel, stirrer, thermometer. Required quantity of maleic anhydride and ethyl alcohol (87%) were transferred to the reaction flask and refluxed for 75 mins. Halfester of maleic acid was formed. The contents of the reaction flask were cooled down and added to it, the required quantity of crotonic acid, vinyl acetate and benzoyl peroxide. The whole contents of the flask was then refluxed at 75-80° for 18hrs. The resulting product was then distilled off to remove unreacted monomers and dried. A solid white resinous substance was obtained. The substance was found soluble in organic substance like ethyl acetate, alcohols, DMF, MEK, THF, cyclohexanone. In order to develop water solubility of the resin it was finally dissolved in ethyl alcohol and then neutralized the residual carboxylic group by treating it with 2-amino-2-methyl-1,3 propanediol. The ratio of ethyl alcohol and AMPD may be 18:1. FTIR spectrum of the product was recorded to ensure the formation of terpolymer. The softening range of the product was 75-80°. The viscosity of dilute solution of the product was measured at 30° using Ostwald type viscometer. Refractive index of the same solutions was determined on refractometer No. 122894 of Zeis Opton (Germany). The product was estimated for C and H on Carlo Erba Mod 1106.

Results and Discussion

Table 1 includes the results of free radical terpolymerisation of maleic anhydride, crotonic acid and vinyl acetate using benzoyl peroxide as initiator.

Terpolymer was characterised by elemental analysis, solubility, I.R. spectral studies, intrinsic viscosity, refractive index etc. The product was estimated for C and H. The elemental analysis of seven samples of the resin contain 43.45 - 55-93% C, 6.88 - 7.0% H and 37.06 - 39.34% 0; crotonic acid contains C=55.8%, H=6.98% and 0=37.2% while the percentage of C, H and O for maleic anhydride are 48.98, 2.04 and

48.98 respectively. The prepared samples of polyvinyl acetate contains C=54.8% H=6.9% and 0=38.3%. This difference in percentage of C, H and O suggests that three monomers participated in the reaction. It is also because these monomers may be polymerised with free radical initiator and growing polymer chains of these monomers couple to produce a new product. The solubilities of these polymers and terpolymers were also tested in different solvents. It may identify and ensure the participation of three monomers in terpolymerisation reaction. Poly (vinyl acetate) and crotonic acid are soluble in toluene whereas the product was found insoluble in toluene. It is noted that the product gets swells in benzene and xylene but slightly in hot toluene. It may be because at the early stage of reaction a part of growing polymer chain of vinyl acetate, crotonic acid or half ester of maleic acid gets terminated before going to terpolymerization resulting polymers of styrene, crotonic acid and half ester of maleic acid. The solubility behaviour supports the results of elemental analysis and characterises the product as terpolymer. The best solvents for terpolymer are cyclohexanone, DMF, acetone, ethyl acetate, alcohols, THF, acetic acid, dioxane etc. FTIR spectral studies has also been carried out (Fig. 1) which provides a concrete evidence that the product was terpolymer. It was observed that the spectra of the polymer is much simpler then monomer itself. This is due to the fact that degree of freedom of vibration is restricted in the polymerization. However the general pattern of the spectra of terpolymer as a rule should show the addition on commutative behaviour of its monomers. The presence of ester carbony absorption band at 1740 cm^{-1}, olefinic = CH band at 3000 cm^{-1} and C-O band at 1240 cm^{-1} (Fig. 1) provides a definite proof that a terpolymer has been formed. Hence all these evidences confirms the formation of terpolymer.

Refluxing of maleic anhydride with alcohol, gives half ester of maleic acid (prepolymer). It is then polymerised with a binary mixture of crotonic acid and vinyl acetate. At the early stage of reaction half ester of maleic acid, crotonic acid and vinyl acetate generate initiating free radicals resulting propagation of growing polymer chains of these monomers. Unreacted monomers and growing polymer chains of each monomer cause mutual termination of growing polymer chains and hence form terpolymer. Mutual termination between same

TABLE 1. SYNTHESIS OF TERPOLYMER OF MALEIC ANHYDRIDE CROTONIC ACID AND VINYL ACETATE AT 75-80°. USING BENZOYL PEROXIDE AS AN INITIATOR FOR 18HRS.

Expt. No.	Monomer in feed MA Mole	CA Mole	VA Mole	Yield g(%)	Estimation C (%)	N (%)	O (%)
1.	0.0948	0.0417	1.0465	40.0	55.83	6.95	37.22
2.	0.0948	0.0694	2.0465	52.0	54.84	6.93	38.22
3.	0.0948	0.1111	1.0465	66.0	53.95	6.91	39.14
4.	0.0948	0.1389	1.0465	70.1	53.78	6.88	39.34
5.	0.0293	0.1111	1.0465	41.0	55.33	6.98	37.69
6.	0.0516	0.1111	1.0465	62.0	55.87	6.99	37.14
7.	0.1379	0.1111	1.465	75.0	55.93	7.01	37.06

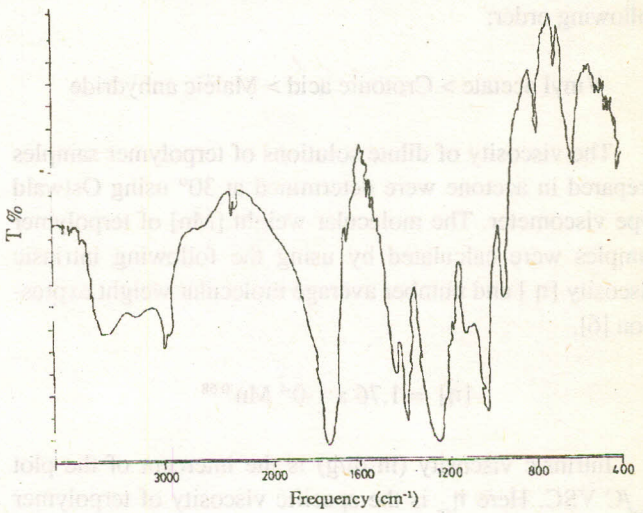

Fig. 1. FTIR Spectrum of terpolymer of maleic anhydride, crotonic acid and vinyl acetate.

TABLE 2. PHYSICAL PARAMETERS OF TERPOLYMER OF MA, CA AND VA.

Expt. No.	[η] dl/g	Mn	Probable number of monomer units in terpolymer Pn MA	CA	VA	Colour	Appearance	Softening range(°C)	Refractive index
1.	0.082	8394	5.0	3	89	White	Solid	70-90	1.3610
2.	0.134	17284	9.6	10	180	"	"	70-90	1.3600
3.	0.132	17906	9.3	15	171	"	"	70-90	1.3610
4.	0.107	12414	7.3	11	125	"	"	70-90	1.3635
5.	0.129	16344	3.5	15	171	"	"	70-90	1.3620
6.	0.140	18434	5.6	17	191	"	"	70-90	1.3610
7.	0.130	16530	13.3	14	163	"	"	70-90	1.3610

monomers radicals form homopolymers of the monomers. The terpolymer so formed contains molecular units of crotonic acid, vinyl acetate and half ester of maleic acid incorporated into each terpolymer molecular chain randomly. The copolymers of crotonic acid and vinyl acetate gives a copolymer of sticky nature but when maleic anhydride in the form of half ester of maleic acid is copolymerised with binary mixture of crotonic acid and vinyl acetate, it gives a nonsticky terpolymer. Further rate of formation of terpolymer (Table 1) gets increased with increasing concentration of half ester of maleic acid at a mole ratio 0.1111:1.0465 of crotonic acid and vinyl acetate. At the mole ratio 0.0948:1.0465 of maleic anhydride and vinyl acetate the yield also increases with increasing concentration of crotonic acid. Keeping the results of elemental analysis, yield and spectral studies into consideration this may be concluded that these three monomers form terpolymer in all monomeric ratios. Further vinyl acetate enters in the growing polymer chain more rapidly than crotonic acid and maleic anhydride (half ester of maleic acid). The order of reactivity of the three monomers may be rather in the following order:

Vinyl acetate > Crotonic acid > Maleic anhydride

The viscosity of dilute solutions of terpolymer samples prepared in acetone were determined at 30° using Ostwald type viscometer. The molecular weight [$\bar{M}n$] of terpolymer samples were calculated by using the following intrinsic viscosity [η] and number average molecular weight expression [6].

$$[\eta] = 1.76 \times 1\text{-}0^{-4}\ Mn^{-0.68}$$

Intrinsic viscosity (in dl/g) is the intercept of the plot η_{sp}/C VSC. Here η_{sp} is the specific viscosity of terpolymer samples ranges 0.082-0.14 dl/g which gives number average molecular weight as 8394-18434. The quantitative treatment of terpolymers sample is very complicated. It is because estimation of functional groups of the reactants involves many experimental problems. Furthermore terpolymerization includes nine propagation reactions, six reactivity ratios and six termination reactions [7]. The terpolymer and multiple composition equations are generally valid only when all of the reactivity ratios have finite values. When one or more monomers is incapable of homopolymerization the equation is generally indeterminate. However keeping into consideration the elemental analysis, yield and number average molecular weight, the probable degree of polymerization (Pn) of three monomers (probable number of monomers units in terpolymer chain, (Table 2) have been calculated [1, 8]. These results indicate major participation of vinyl acetate monomer units (Pn = 89-191) in the formation of terpolymer as compared with maleic anhydride (in the form of half ester of maleic acid) Pn = 5-13.3. and crotonic acid (Pn=3-17). The rate of addition of maleic anhydride and crotonic acid monomer units gets increased with increasing their concentration in feed. At a feed of 7.57 mole % maleic anhydride (MA), 8.9 mole % crotonic acid (CA) and 83.5 mole % vinyl acetate, a terpolymer of the following type may be proposed.

$$\sim\sim (MA)_{93}\text{——}(CA)_{15}\text{——}(VA)_{17} \sim\sim$$

Terpolymer samples are white nonsticky resinous substance soluble in organic solvents like DMF, THF, alcohols, MEK, ethyl acetate. The refractive index of terpolymer was found to be 1.3610–1.3635. This terpolymer may be used in the preparation of hair spray. The hair spray formulated with this terpolymer produce a thin film superior in clarity, gloss and manageable and also less tacky. On the other hand the hair sprays based on a copolymer of vinyl acetate and crotonic acid show many inadequencies such as inadequate clarity of films, manageability and gloss as well as undesirable flaking. The maximum inadequecies may be removed by using this product (terpolymer) [1]. All terpolymer samples first start softening at 70-90° and this decomposes at 104-106°. When the temperature reaches at 130°, the substance converts into transparent liquid and distills off at 136-170°.

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