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Gel Permeation Chromatography for Characterization of Graft Copolymer

K. S. V. Srinivasan and D. Sudhakar

Polymer Division, Central Leather Research Institute, Madras-600 020, India

SUMMARY

The present paper describes the grafting of vinyl monomers onto cellulose nitrate in non-aqueous medium using benzoyl peroxide as a catalyst. The complete separation of the homopolymers and graft copolymer was carried out by selective solvent extraction. The graft copolymer was characterized by IR spectra. The GPC was used as a technique to differentiate between homopolymer, polymer mixture, polyblend,and graft copolymer.

INTRODUCTION

Lacquers based on cellulose nitrate have been extensively used in surface coating industries (1,2). The modification of cellulose nitrate for this purpose has been achieved by using external plasticizers like dibutylphthalate, dioctylphthalate etc.(1). The drawback with the plasticization by small molecule is its migration on ageing and making the film brittle. Grafting of vinyl monomers onto cellulose nitrate initiated by benzoyl peroxide has been suggested as a potentially good means of altering the properties of the base polymer (3). The present communication deals with the study as to whether Gel permeation chromatography can be used as a tool to differentiate between graft copolymer, polyblend, homopolymer, and polymer mixture.

EXPERIMENTAL

Cellulose nitrate (1/2 sec) (Ashahi Chemical Industry Ltd., Japan), methyl methacrylate (Rohm&Haas, Philadelphia), benzoyl peroxide (B.D.H.) were used in the present study. Graft copolymerization was carried out by taking a calculated amount of cellulose nitrate (1.o g)with 1o.o ml methyl isobutyl ketone in a polymerization reaction tube. Monomer 1.o ml and initiator solution (2.5 ml of 5% solution) were added to it before purging with purified nitro-

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gen for about 15 minutes. Then the reaction tube was sealed and heated to a constant temperature of 7o +/- o.1°C. After the reaction time of about 3 hours, the tube was removed from the bath , cooled in ice, and the contents were precipitated with excess of petroleum ether (6o-8o°C). The gross polymer was filtered and dried to constant weight in vacuo at 6o°C. The polymer obtained contains homopolymer, graft copolymer, and the base polymer, which were separated as follows:

The polymer was soxhlet extracted with benzene to remove the polymethyl methacrylate homopolymer, then with methanol to remove the base polymer (cellulose nitrate), and the remaining material is a true graft copolymer. Poly (methyl methacrylate) homopolymer was also prepared by polymerizing methyl methacrylate using benzoyl peroxide as initiator at 7o°C.

RESULTS AND DISCUSSION

The infrared spectra of cellulose nitrate and the cellulose nitrate-g-poly (methyl methacrylate) are shown in Fig.1. Fig.1a shows the infrared spectrum of cellulose nitrate characterized by a broad medium hydroxyl band at 34oocm^{-1}, a weak absorption at 29oocm^{-1} indicating a small number of C-H linkages, and by covalent O-NO$_2$ asymmetric and symmetric stretching vibrations at 128ocm^{-1} and at 1655cm^{-1}. Fig.1b gives the IR spectrum of pure graft copolymer completely separated from homopolymers. It shows the characteristic peaks of poly (methyl methacrylate) apart from the peaks due to cellulose nitrate. This indicates that the poly (methyl methacrylate) chains are attached to the cellulose nitrate base polymer.
Gel permeation chromatograms were obtained on a high pressure liquid chromatograph (Waters Associates Model 244), using dilute polymer solutions (o.o2%) in tetrahydrofuran and a flow rate of 1ml/min. The chromatograph was equipped with four micro styragel columns in series (pore size:1o^6,1o^5,1o^4,1o^3 Å). Elution volumes are proportional to the molecular weights of polymers (4). When samples of poly (methyl methacrylate) and cellulose nitrate which differ in molecular weights were recorded independently, peaks in elution volume could be observed at different positions in the Gel permeation chromatogram. In the present case peaks in elution volume at 62.5 for poly (methyl methacrylate) and at 87.5 for cellulose nitrate were observed. A mixture of poly (methyl methacrylate) and cellulose nitrate of the same ratio as that of graft copolymer was recorded and two peaks in elution volume were again observed at the identical positions as those of the constituent homopolymers. This shows that the constituent polymers retain their iden-

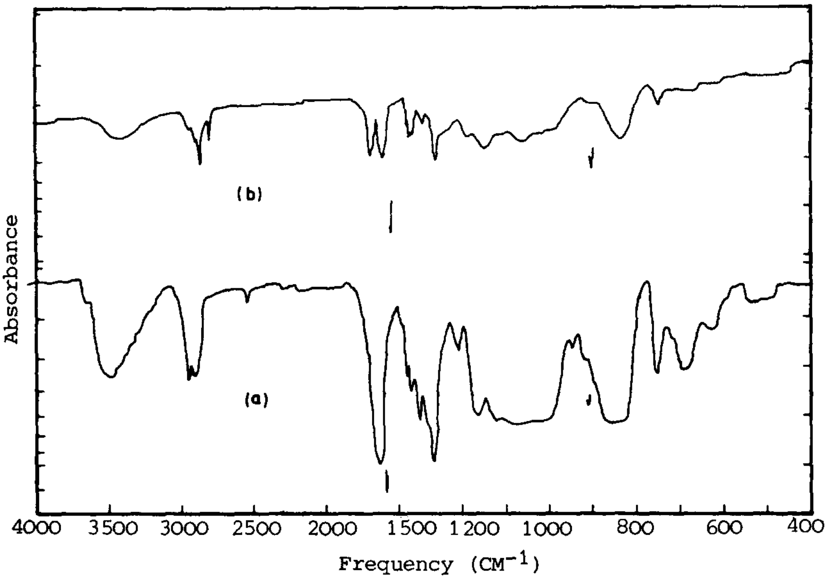

Fig. 1. IR spectra of (a) cellulose nitrate. (b) cellulose nitrate-g-Poly(methyl methacrylate)

tity in a physical mixture. Further, a true polyblend formation may also be ruled out, as a single peak in elution volume is to be observed with a shift of the peak in elution volume, which may be in between the constituent homopolymers. When an isolated graft copolymer was recorded, a single peak in elution volume at 8o.o with a little shift to cellulose nitrate (base polymer) was observed. Due to poly (methyl methacrylate), the second peak in elution volume is absent in spite of the evidence of poly (methyl methacrylate) attached to cellulose nitrate, as revealed by infrared spectrum.

Thus, the results indicate that GPC can be used as a technique to differentiate between homopolymer, polyblend, physical mixture, and graft copolymer. Further work with various systems, which may support our above statements, is in progress.

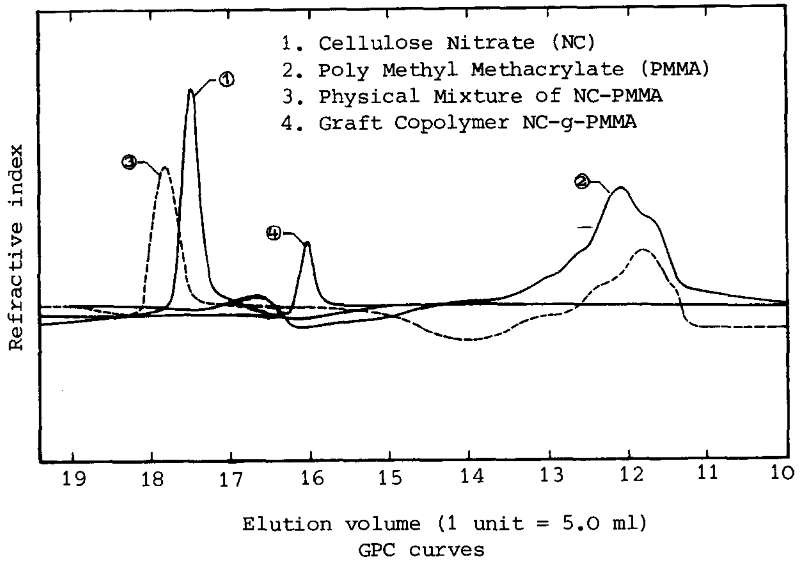

Fig. 2

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