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Grafting of side chain liquid crystal monomers onto polyethylene film

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Abstract

In order to obtain films of liquid crystalline polymers, a commercial polyethylene films was grafted with acryloyl chloride using γ-irradiation, and two tolane-containing alcohols were reacted with the chloride to obtain the corresponding acrylates. The morphology changes were studied by DSC, X-ray diffractometry and optical microscopy. The crystallinity of polyethylene films decreased by grafting, and mesophase with spherulites was observed over a wide temperature range.

INTRODUCTION

There are a great number of studies on side chain liquid crystal(LC) polymers which consist of flexible main chains to which mesogen groups are linked through spacers. When these polymers are used for display devices in the form of thin films, reasonably high molecular weight is required for their mechanical strength. This means high viscosity, and therefore response of phase changes becomes slow compared to that of corresponding low molecular weight LCs. Alternative materials, in which low molecular weight LCs are dispersed in host polymers, have been used as optoelectronic displays(1) and separation membranes(2).

An alternative method for obtaining LC-containing films is grafting LC polymers onto the surface of thin films of amorphous polymers. In such cases the molecular weight of grafted LC polymer may not be high because of the polymer films provide mechanical strength. Depending on applications, the flexibility of films offers many different shapes.

Grafting various vinyl monomers onto various polymer thin films by γ-ray irradiation has been studied by many researchers(3). In this work a few mesogen-containing acrylic polymers were grafted onto a low density polyethylene (LDPE) film by γ-irradiation, and the products were characterized by means of differential

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precipitated solid was filtered, washed with water and dried. Recrystallization from acetone/ethanol mixture gave **4-[carbo(12-hydroxy)dodecyloxy] tolane** (**4a**) as a white crystalline powder with 30% yield. A similar result was obtained in the case of 4'-*n*-heptylphenylacetylene which was synthesized from 4'-n-heptylacetophenone treated with phosphorus pentachloride followed by dehydrochlorination with lithium n-butylamide in methylsulfoxide.

Grafting: The above tolanes were reacted with acryloylchloride in order to obtain the acrylate. However, premature polymerization took place and the desired monomers could not be obtained. Therefore, grafting of acryloylchloride followed with esterification was carried out. The direct grafting was performed by irradiation LDPE (PEMEX product with crystallinity 62%, Mn 34,000) film(1 x 5 x 0.0008 cm) soaked in toluene solution of acryloyl chloride (60 wt.%) in a Pyrex tube. The system was degassed by repeated freezing and thawing, and sealed under vacuum. The system was then irradiated with Co^{60} γ-ray, with a dose rate of 5.1 kGy/h. Vapor phase grafting in a degassed ampoule saturated with acryloyl chloride vapor was also carried out with the same irradiation intensity. The unreacted chloride and its homopolymer were removed by chloroform extraction. The grafting yield was determined gravimetrically after esterification of acryloyl chloride with methanol.

Esterification: The PE films thus grafted with acryloyl chloride were placed in a solution of dichloromethane in which required amounts of the mesogenic alcohol and triethylamine were dissolved, and the mixture was stirred gently for 24 hrs. The film was then washed with dichloromethane and dried in vacuum.

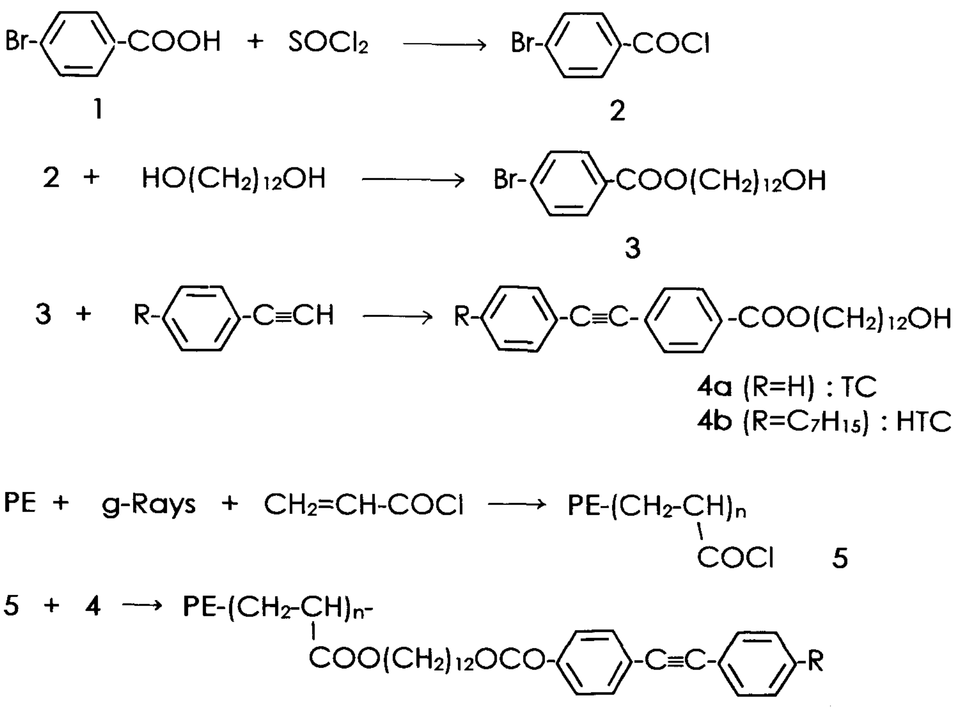
Characterization: DSC was performed under nitrogen flow using a du Pont 2100. X-ray diffractometry was done using a Siemens D-500 diffractomer with Cu-K_α radiation of 1.540Å. The crystallinity degree of grafted PE films was calculated by using a program SOCABIM V 3.0 1986, 1991-Copyright Siemens 1991. FT-IR spectra were taken using a Perkin Elmer Model 1600 spectrophotometer fitted with an attenued total reflection (ATR) mode. A polarized optical microscope, Olympus BH-2, fitted with a Linkam heating plate was used for microscope observations.

RESULTS AND DISCUSSION.

Observation under a polarized optical microscope of the tolane carboxylate (TC) revealed a crystalline phase change over a temperature range from 70 to 112 °C during which flow of bâtonnets was observed. The material melted at 115 °C , and on cooling the melt crystallized at 81°C forming circumferential fans with cracks. In the case of hexyl tolane carboxylate (HTC) the crystal phase change and melting was observed at 72 and 80 °C, respectively, but unexpectedly mesophase was not observed. Figs. 1 (a) and (b) show DSC curves for TC and HTC. The first endotherms (71.4 and 79.7 °C for TC and 68.3 °C for HTC) are attributed to the crystal phase change, and the second and larger endotherm (108 thermal analysis and polarized optical microscope. The preliminary results are described in this report.

EXPERIMENTAL

Synthesis: The synthetic route is shown in Scheme 1. **4-Bromo-(12-hydroxy)dodecyl benzoate(3)** was obtained by esterification of **4-bromobenzoyl chloride(2)** (0.137 mole) with 1,12-dodecandiol (0.105 mole) in pyridine (300 ml) at room temperature for 72 hrs with stirring under nitrogen. The reaction mixture was poured into dilute hydrochloric acid, the precipitated solid was filtered, and repeatedly washed with water. The product was extracted with toluene and a white powder melting at 49-50°C was obtained with 54% yield by evaporation of toluene under reduced pressure. *Elemental analysis:* Found: C: 57.19%. H: 6.96%; Calcd. for $C_{19}H_{29}O_3Br$, C: 59.21%, H: 7.60%.



Scheme 1. Synthetic route for PE grafted with tolane-containing acrylates.

In a 50 mL flask containing pyridine(30 mL) and triethylamine(20 mL) placed under nitrogen flow were placed compound **3** (10 g, 0.026 mole), phenylacetylene (5 ml, 0.051 mole), triphenylphosphine(TPP) (0.1 g), CuI(0.1 g) and $PdCl_2(TPP)_2$ (0.1 g), and the mixture was stirred under nitrogen at 65-70°C for 24 hrs. The reaction mixture was then poured into dilute hydrochloric acid, and the for TC and 79 °C for HTC) to melting. Apparently neither TC nor HTC exhibited stable mesophases.

A commercially available PE film (PEMEX product, thickness 0.08 mm) with crystallinity of 62% and Mn of 34000 was used for grafting of acryloyl chloride, followed by esterification with TC and HTC. FT-IR spectra of the grafted films showed peaks due to C≡C (2160 cm^{-1}), COO (1706) and aromatics(1600). The crystallinity of the grafted PE films decreased with increase in grafting yields. For example, the crystallinity of the PE film decreased to 34% from its original 62%

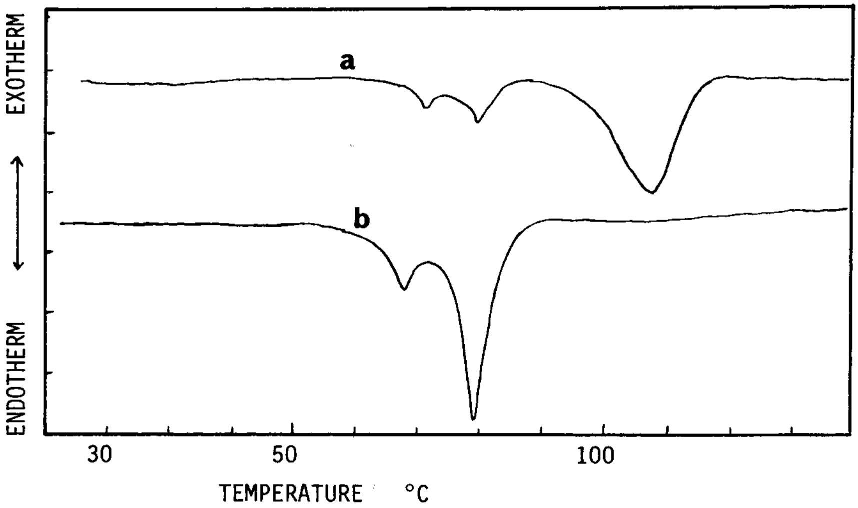


Fig. 1. DSC of TC(**a**) and HTC(**b**). Heating rate: 10°C/min.

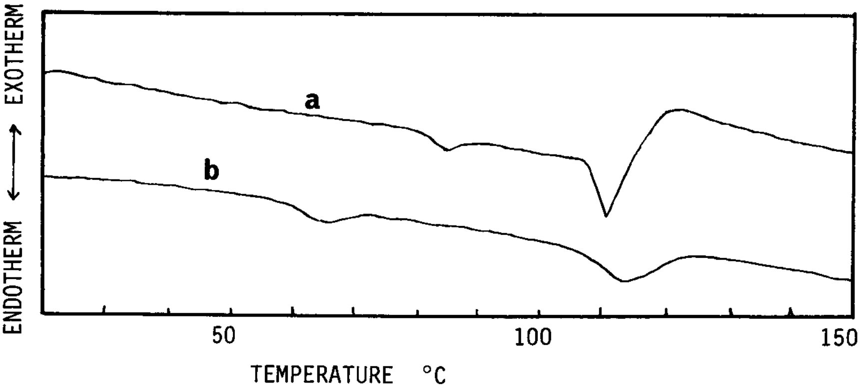


Fig. 2. DSC of PE films grafted with TC acrylate. 40.7 % graft (**a**), 48.5% graft (**b**), Heating rate: 10 °C/min.

upon 120% grafting. The glass transition temperature of the grafted PE films also decreased by grafting as shown in Fig. 2; from 85 to 64 with increase in grafting from 41 to 485%.

The high temperature endotherm of the films did not change appreciably, being in the region of 110.5 - 112.2 °C independent of the grafting percentage. Under a polarized optical microscope, a frozen texture of crosses (spherulites) dispersed in the amorphous polymer characteristic of nematic phase, was detected over the temperature range from ambient to 111-112 °C at which temperature the birefringence disappeared. On cooling from this temperature, the birefringence in the form of spherulites reappeared. This endotherm is due to melting of PE film which destroys the mesophase formed by the lateral groups of the grafted acrylate.

In the case of HTC-grafted PE films also, the crystallinity of the PE film decreased by grafting; e.g, from 62 to 34% by grafting of 128%. DSC curves also showed two transitions, similar to the case of HTC-grafted PE, as shown in Fig. 3. The first one at the low temperature range (20-35°C) corresponds to the Tg of the parts of the PE films grafted with the polyacrylate, and the second at around 110°C corresponds to the melting of PE. Over the temperature range between the Tg and the Tm of PE, a mesophase showing aligned spherulites was observed for these HTC-grafted PE films. The birefringence disappeared with melting of the PE . but it reappeared on cooling.

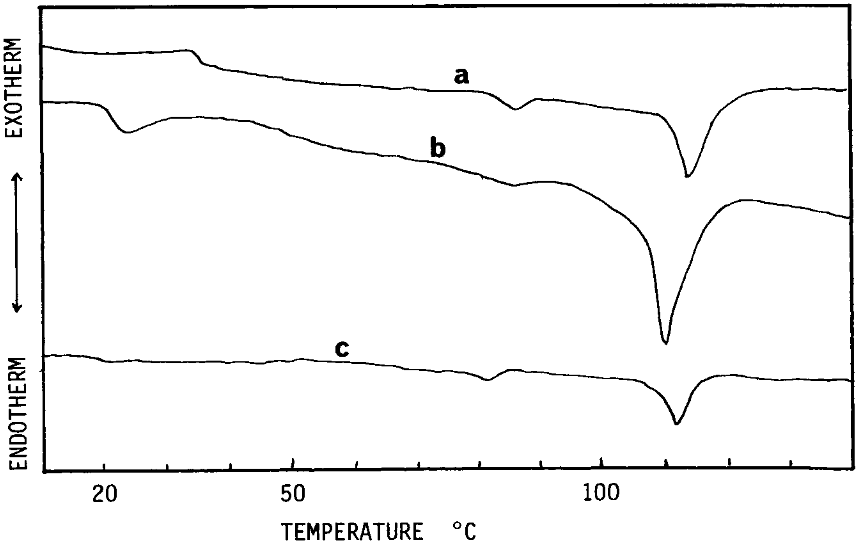


Fig. 3. DSC of PE films grafted with HTC acrylate. 44% graft (**a**), 100 % graft (**b**), 128 % graft (**c**). Heating rate: 10 °C/min.

It is interesting to note that the tolane carboxylate itself does not form LC phase but it does over a temperature range from room temperature to 110°C when grafted onto a PE film. The hydroxy group of the alcohols is probably the cause of the difference; the absence of hydroxy groups makes the mesophase stable for the grafted polymers. It was shown by this study that LC polymer films can be readily obtained by grafting mesogen-containing polymers onto polymer films such as PE.

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