

Synthesis of Poly(ethylene-block-vinylalcohol)for Use as Amphiphilic Film Surface at High Temperature

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Poly (ethylene-block-vinyl alcohol), which consisted of both hydrophobic and hydrophilic blocks, was prepared by using polyethylene single crystals as starting material. Polyethylene single crystals reacted with fuming nitric acid resulting in long methylene chains with functional groups such as COOH and NO₂ at the ends (the chain length were almost same as the lamellar thickness of polyethylene single crystal). The functionalized methylene chains were allowed to react with 4-aminostyrene to give corresponding amides, i.e., methylene chains with vinyl groups at the ends (macromer). The macromers were extended by block-copolymerization with vinyl acetate, then saponified resulting in PE/PVA block co-polymer.

The block copolymer was molded into sheets which were subsequently heat-treated in contact with hydrophilic or hydrophobic media. Depending on the media, the sheet surface changed at high temperature reversibly from hydrophilic to hydrophobic and vice versa. The surface property was fixed by quenching because both blocks were able to crystallize. Thus the surface of this material can be tailored for various purposes at high temperature, and then used in stable at room temperature.

1. INTRODUCTION

Surface properties of polymer solids are strongly dependent on the chemical composition and structure of the polymer surface. It has been generally accepted that UV-photon and plasma interact with polymer chains, which generate a variety of oxygen-containing functionalities at the polymer surface. However, the properties thus generated can not convert reversibly. In this study we developed a material which was amphiphilic at high temperature, i.e., the surface properties could be reversibly controlled by the environmental treatment at high temperature, but they can be fixed at room temperature. In order to stabilize the resultant properties, components at the polymer surface are requested to be crystalline or in glassy state at room temperature. In this study we synthesized block-copolymers, which consisted of both hydrophobic and hydrophilic blocks. As hydrophobic blocks, methylene chains

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of about 10nm length were used. However, it is difficult to produce such long hydrocarbon blocks by the conventional chemical technique, so we used polymer single crystals as starting material for the synthesis of hydrophobic blocks. As hydrophilic blocks, polyvinyl alcohol blocks with OH's were introduced. Sheets were produced with the block copolymers, and heat-treated in contact with various media, while their physical properties reversibly converted at high temperature. As both blocks are crystallizable at room temperature, the resultant surface morphology, i.e. its surface property, was stable at room temperature.

2. EXPERIMENTAL

2-1 Preparation of PE/PVA Block Copolymer

2-1-1 Long Chain Hydrocarbons with Functional Groups at their Ends

Polyethylene was dissolved in xylene at 130°C at concentration of 1wt%, then isothermally crystallized into lamellae at 88°C. Polyethylene chains in the crystalline region oriented perpendicular to the lamellae, and at the lamellar surface, they were folded back and forth [1]. As the folded parts bear much stress, they were preferentially cut by oxidation with fuming nitric acid at 80°C [2]. Weight of PE single crystals decreased with the fuming nitric acid treatment time and finally saturated to 88 wt% of the original weight. IR showed that functional groups such as COOH and NO₂ were introduced on the lamellar surfaces, (1).

2-1-2 Determination of Methylene Chain Length

Polyethylene oligomers functionallized with COOH or NO₂ at their ends (f-PE) were obtained by dissolving the lamellae in xylene. f-PE was dissolved in *o*-dichlorobenzene and measured the molecular weight distribution at 140°C using GPC (Waters Co., 150CV plus) in which 2 columns were connected in series. Gel in the columns was cross-linked styrene-divinylbenzene. Two kinds of gels with pore diameter of 50 nm and 10nm were used for characterization of the f-PE. GPC of the samples is shown in Fig.1 as a function of the treatment time. Longer molecules flow faster and came out earlier. With samples treated for 12hr, two peaks are observed. With longer treatment time, the peak at smaller elution time became weaker but that at larger elution time stronger. Molecular weight corresponding to smaller elution time was almost twice that of the longer elution time. After 120hr, the latter only survived. This final chain length was close to the single crystal thickness. It was proven that almost constant chain length was obtained by cutting off all folding parts on PE single crystal surface. From this fact, the sample of treatment time 120hr was used for the synthesis of macromer in the following.

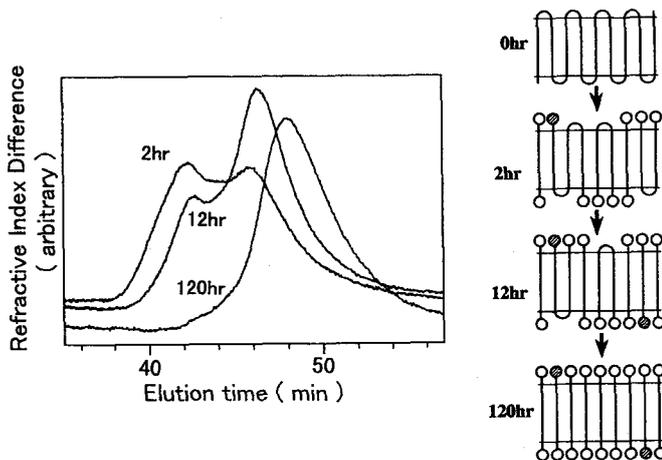


Fig.1 GPC of polyethylene single crystals treated with fuming nitric acid. Treatment time is 2hr, 12hr and 120hr.

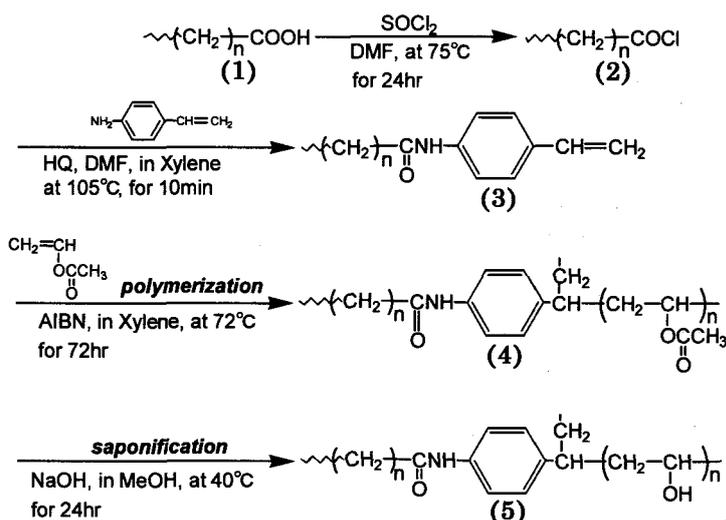
2-1-3 Introduction of Vinyl Groups at f-PE Ends

To extend f-PE with vinyl groups, f-PE was reacted with p-aminostyrene. IR suggest that f-PE did not always have COOH's at their ends but also NO₂. Though f-PE chain ends terminated with NO₂ remained without vinyl groups, such unfruitful stems could be removed using solubility difference. Therefore we will discuss here only on the method of introducing vinyl group via COOH.

Thionyl chloride was added to (1) at 75°C with a small amount of DMF to change COOH to COCl. After the reaction for 24hr, excess thionyl chloride was removed by vacuum distillation. The product (2) was dissolved in xylene, and 4-aminostyrene, DMF and hydroquinone (as an inhibitor) were added, and was kept at 120°C for 1hr. The reactant was expected to be a mixture of di- mono-vinyl substituted macromers (3) and f-PE without vinyl group.

2-1-4 Radical Polymerization of Vinyl Acetate from Vinyl End Group of Macromer

The mixture (3) was dissolved in xylene in a separable flask at 105°C. After replaced with argon, the flask was cooled down to 72°C. Purified vinyl acetate was added to with a small amount of AIBN as an initiator, then reacted at 80°C for 72hr. The reactant was put in methanol, filtrated, and washed several times with methanol, (4). IR showed that the filtrated contained homopolymer of vinyl acetate, and the residue was composed of block copolymer and the non-reacted f-PE. In order to extract the non-reacted f-PE, the residue was put in hot xylene (120°C) for 10hr. IR showed that most non-reacted f-PE was extracted from the residue.



Scheme Synthesis of amphiphilic PE/PVA block copolymer

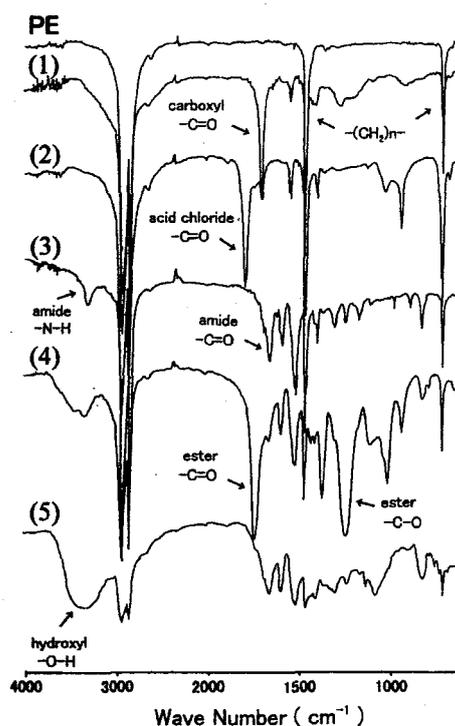


Fig.2 FT-IR spectra of the compounds during whole reactions. Each spectrum is correspondent with the chemical compound in scheme

2-1-5 Saponification of the block copolymer

The block copolymer was put in methanol, 40%NaOH aqueous solution was added and was heated to 40°C [3]. Reaction was carried out for 24hr under stirring. The reactant was washed with methanol and distilled water, and dried. By this procedure IR absorption due to ester group of PVAc disappeared, instead that of OH appeared. Thus block copolymer of PE/PVA (5) was prepared.

2-2 Preparation and Surface Treatment of the Block Copolymer Sheet

The block-copolymer was sandwiched with Teflon sheets and was put in a press-forming machine, which was preheated to 170°C. Firstly, it was heated for 10min without pressure, pressed at 100kg/cm², and then the pressure was released for air ventilation. This process was repeated 3 times, and finally applied 100kg/cm² for 10min and cooled down to room temperature. Thus a flat sheet was obtained.

Glycerin and xylene were used as contacting media for hydrophilicity and hydrophobicity respectively. In glycerin, the treatment was carried out at 120°C, then cooled down, rinsed with water in order to remove glycerin from the sheet surface. For the xylene treatment maximum temperature was at most 70°C because of softening of the sheet. Since xylene was volatile, the treated sheets were dried under vacuum. In order to avoid deformation of the sheets during the heat treatment, sheets were sandwiched with Teflon or polyester films for hydrophilicity and hydrophobicity respectively, and were pressed at a pressure of 10kg/cm² at 130°C for 10min for various treatment time.

2-3 Contact Angle Measurement of a Water Droplet on the Sheet

Distilled water was dropped on the treated sheets. Contact angle of the droplet was measured using a contact angle meter (Kyowa interface science Co., CA-D type).

3. RESULTS AND DISCUSSION

3-1 Crystallinity of the Block Copolymer Sheet

X-ray diffraction of the sheet of PE/PVA block copolymer is shown in Fig.3. Crystalline peaks by PE and PVA crystallites are clearly observed. Upon heating above 250°C these diffraction peaks smeared out but reappeared on cooling. So it was concluded that these block components conformed crystalline regions of PE and PVA respectively at room temperature.

3-2 Dependence of Surface Property of Block Copolymer Sheets on Heat Treatment Condition

Fig.4 shows contact angle of a water droplet on the sheet surface. The value of 110° at beginning is due to hydrophobic property of the sheet as-molded between Teflon films. By heat treatment in glycerin at 120 °C. The contact angle decreased to

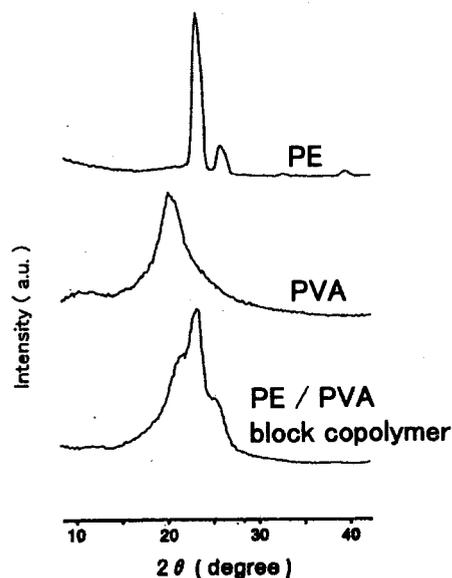


Fig.3 Diffracted X-ray intensity profile of PE/PVA block copolymer

near 70° suggesting that the surface became hydrophilic. For recovering the surface to hydrophobicity, the sheet was dipped in xylene at 70°C , but the contact angle increased only by 10° but not up to 110° . Repeating treatment for hydrophilicity in glycerin, the angle reached 70° again. Recover of the contact angle by the hydrophobic treatment in xylene at 70°C became smaller and smaller with the repetition. It was because we adopted 70°C , as the treatment temperature for hydrophobicity, above which the sheet became too soft to keep the original form in xylene. As the melting points of PE and PVA are much higher than 70°C , consequently both components actually could not exchange their positions during the xylene treatment. On the other hand, during the heat treatment in glycerin at 130°C , PE blocks were in melt so PE blocks were mobile (though PVA blocks are still in crystalline state) and could come out to the surface from behind PVA crystalline block, improving hydrophilicity only in one way. In order to increase the segmental mobility during hydrophilic treatment, we have treated the sheet between solid films.

Fig.5 shows the surface properties of the sheets heat-treated between solid films. Heat treatments for hydrophilicity (sandwiched with PET) and for hydrophobicity (sandwiched with Teflon) were repeatedly carried out at 130°C for several minutes and quenched it. In this case, recovery of the contact angles was achieved on both treatments toward hydrophilicity and hydrophobicity. Here the surface properties once created at 130°C were hold at room temperature.

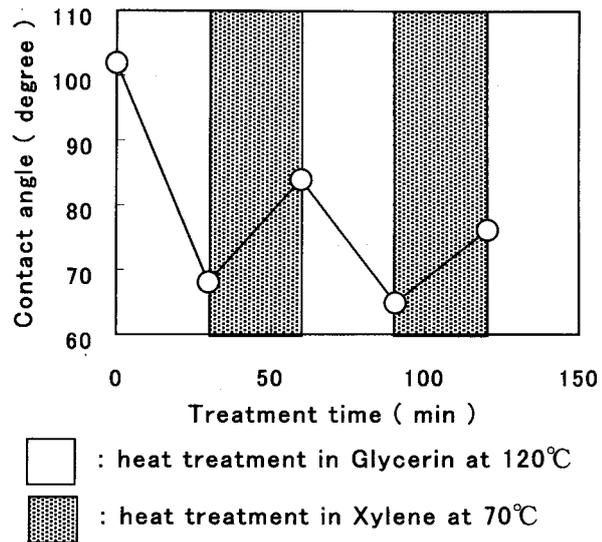


Fig.4 Change of a water droplet contact angle on PE/PVA block copolymer sheets by repeated heat treatment in glycerin at 120°C and in xylene at 70°C .

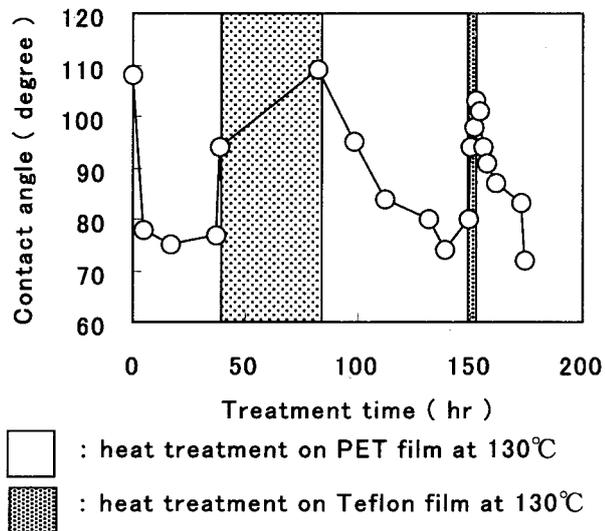


Fig.5 Change of a water droplet contact angle on PE/PVA block copolymer sheets by repeated heat treatment between PET and Teflon films at 130°C .

3-3 Morphologies of the Hydrophobic and Hydrophilic Surfaces

Fig.6 shows the sheet surfaces taken by the scanning probe microscope. The left one (a) was the surface heat treated on PET film (hydrophilic) at 130°C and the right one (b) on a silicon single crystal (hydrophobic). On Fig.6a, "edge on" view of crystalline lamellae of PE macromer is clearly observed with a repeating distance of ca.14nm, i.e., on hydrophobic treatment PE block appeared on the surface and crystallized forming lamellae. On the contrary, rather larger entities are observed on the surface after hydrophilic treatment. As the melting temperature of PVA is much higher than the treatment temperature, PVA crystallites once produced on sheet formation did not melt during the repeated heat treatments. Instead the mobile PE blocks hid behind the PVA crystallites, resulting in hydrophilic sheet surface.

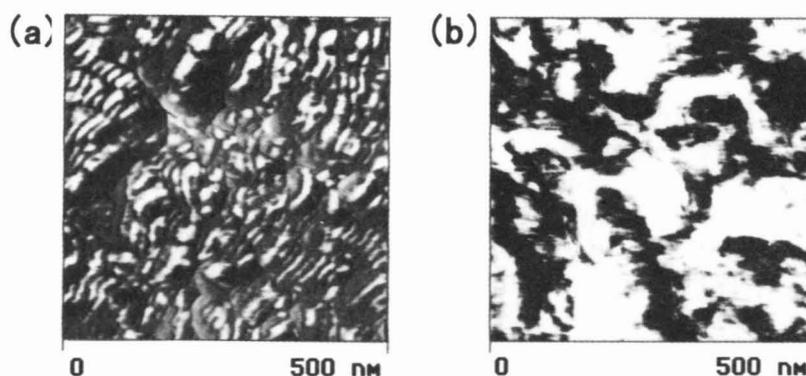


Fig.6 Scanning probe microscopic image of PE/PVA block copolymer sheet surfaces. (a) hydrophobic surface, (b) hydrophilic surface (taken in the phase shift mode).

4. CONCLUSIONS

By fuming nitric acid treatment of PE lamellar crystal, long methylene chains with COOH at the ends was produced. By extending the chain ends with 4-aminostyrene via amide link, macromers terminated with vinyl groups were synthesized. Vinyl acetate was block-co-polymerized from the vinyl groups. PE/PVAc block co-polymer was subsequently saponified to PE/PVA block co-polymer. As PE block is hydrophobic but PVA block is hydrophilic, this block copolymer is amphiphilic at high temperature. Consequently the surface morphology can be intentionally controlled by choosing various kinds of ambient media. The resultant morphology is fixed at room temperature because both blocks are crystalline at room temperature.

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