with evaporation of the solvent and thus monomolecular particles cannot be obtained. This small number of particles in the spray method highly restricts observations other than TEM. On the other hand, in a recent work, particles obtained on a water surface were collected to cover about 60% of the water surface by moving the compressing barrier and accumulated on a substrate by touching it to the water surface repeatedly.[12] Thus the number of particles obtained per unit area of the substrate is much larger than that in spray method. Thus this method is suitable not only for TEM observation but also for measuring other physical and chemical properties of particles. As mentioned in the Introduction, monomolecular particles are considered to have interesting properties from two standpoints. The first is that they consist of one molecule. Therefore, they are free from intermolecular entanglements, which are essential for polymer solids. This is an extraordinary state, thus the properties are interesting. The second is the small diameter of the particles, which is not easily obtained by other methods. (By decreasing the molecular weight of the polymer, it may be possible to obtain smaller particles than those studied in this paper. However, this was not tried because of the limited resolution of TEM.) With decreasing diameter, the surface area per unit volume becomes larger. Thus the surface properties will become dominant and detectable. Therefore, these particles are considered to be suitable materials to study surface properties of polymers.

IV. Conclusions

The ultrafine particles obtained by spreading dilute polystyrene solutions in benzene on a water surface are monomolecular particles because (1) with decreasing concentration of starting polymer solution, the diameter distribution of obtained particles became sharper and converged to limiting value; (2) a dependence of diameter on molecular weight was clearly observed; (3) a good fit was obtained between observed diameter distributions and those calculated from molecular weight distribution data measured by GPC; (4) particles from the mixed solution containing polystyrenes of two different molecular weights had a bimodal diameter distribution, each peak corresponding to a diameter distribution of a component polystyrene; and (5) the measured thickness of the particles was consistent with the value calculated by assuming bulk density.

Acknowledgment. I wish to thank Prof. Takeji Hashimoto, Kyoto University, for valuable discussion. Thanks are also due to Prof. Naoya Ogata and Prof. Kohei Sanui, Sophia University, for their encouragement.

Registry No. Polystyrene, 9003-53-6.

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(11) From the data sheet of Toyo Soda. Measurements were made in tetrahydrofuran at 25 °C on a Toyo Soda HLC-802UR GPC apparatus. A UV spectrometer was operated as a concentration detector, and four TSK-GEL G6000H6 columns were used, each of which was 60 cm in length and 7.5 mm in inner diameter, packed with polystyrene gel particles with a porosity of 10^6 Å. The number of theoretical plates was more than 6000 plates/ft. The injection was 0.5 mL, and sample concentration was 0.2 mg/mL. Flow rate was 1.0 mL/min.
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pH-Induced Regulation of the Permeability of a Polymer Membrane with a Transmembrane Pathway Prepared from a Synthetic Polypeptide

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ABSTRACT: A novel polymer membrane having a transmembrane permeating pathway ("channel") was prepared from a synthetic polypeptide by using the newly synthesized poly(butyl methacrylate)–polypeptide graft copolymer as the material. The transmembrane continuous phases of the hydrophilic polypeptide were suggested to be formed in the stable matrix from vinyl polymer and to function as a permeating pathway for polar substances. The infrared spectra of the membrane showed the pH-dependent conformational change of the polypeptide segment. Regulation of the permeability was performed by pH based on the conformational change of polypeptide composing the pathway.

Introduction

Membrane proteins, distributed like a mosaic in the phospholipid bilayer, play important roles in the life process, including the transport of substances, metabolism, and the transmission of information. Some of the membrane proteins are considered to form a "hole" or a "channel" for transporting a specific substrate across the membrane and control the permeability by conformational change corresponding to external stimuli.

Numerous model systems from polymer membranes have been reported, which mimic the function of biomembrane. As for the specific, facilitated, and/or active transport, cation- or anion-exchange polymers,[1] a crown ether containing polymer,[2] a polymer carrying lactone derivatives,[3] and polymers incorporating moieties that undergo reversible isomerization, such as the *N*-hydroxy-

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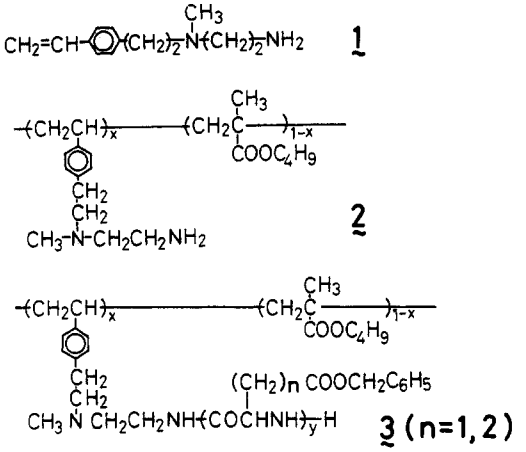
Chart I



ethyl group,[4] have been examined.

Recently, we have prepared a new biomembrane model from a synthetic macromolecule, which has the synthetic polypeptide microdomain as a membrane protein model.[5] The design of the membrane material was based on the synthesis of vinyl polymers with a polypeptide branch, i.e., polyvinyl–polypeptide graft copolymers. As the backbone was adopted poly(butyl methacrylate), which is known to have an excellent mechanical property. The branch was composed of a hydrophilic polypeptide such as poly(L-aspartic acid). It is known that conformational change of synthetic polypeptides occurs by the information of the surroundings including pH, ions, chemical substance, temperature, solvent composition, etc. It is expected that solute permeability can be controlled by the conformational change of polypeptide segment in the membrane responding to these external stimuli.

In a previous communication,[5] we showed the preliminary result of ion transport across the membrane from poly(butyl methacrylate)–poly(L-aspartic acid) graft copolymer. The continuous phases of polypeptide were suggested to be formed in the membrane and to function as a permeating pathway for ions (transmembrane channel). The channel-composing polypeptide segment in the membrane showed the pH-induced reversible conformational change that would influence the ion permeability.

The present paper will describe the results of our more intensive study on the pH regulation of permeability of the membranes prepared from a series of newly synthesized poly(butyl methacrylate)/polypeptide graft copolymers. L-Glutamic acid and L-aspartic acid were used as components of the polypeptide branch. In order to observe the change in permeability with pH independently of the direct effect of the dissociative groups of polyelectrolyte domain in the membrane, styrene glycol, a water-soluble nonelectrolyte convenient for spectrophotometric determination, was adopted as the permeating substance.

Experimental Section

Materials. *N*-Methyl-*N*-(4-vinylphenethyl)ethylenediamine (1) (Chart I) was synthesized by the addition reaction of *N*-methylethylenediamine with 1,4-divinylbenzene catalyzed by lithium alkylamide.[6] Butyl methacrylate (BMA) was distilled over calcium hydride. β-Benzyl L-aspartate *N*-carboxylic anhydride (BLA–NCA) and γ-benzyl L-glutamate *N*-carboxylic anhydride (BLG–NCA) were prepared by the reaction between β-benzyl L-aspartate or γ-benzyl L-glutamate, respectively, and a benzene solution of phosgene.[7] A 0.1 N sodium chloride solution and styrene glycol were those commercially available. Benzene, dichloromethane, hexane, and tetrahydrofuran (THF) were purified by the usual methods. The other chemicals used were of reagent grade.

Copolymerization of 1 and Butyl Methacrylate. Synthesis of Backbone Copolymer 2.[8] The radical copolymerization of 1 (0.3–1.7 mmol) and butyl methacrylate (31.7 mmol) was carried out in a sealed glass ampule at 45 °C with 2,2′-azobis(2,4-dimethylvaleronitrile) as initiator (0.06–0.17 mmol) and benzene as solvent (30 mL). After a definite period of time (14 h), the ampule was opened, and the content was poured into a large excess of cold (2–3 °C) hexane (750–1000 mL). The precipitated polymer was redissolved in benzene and subjected to freeze-drying to give a white solid in a 45–55% yield. The content of 1 in copolymer 2 was determined from the area ratio of the signal of $-COOCH_2-$ of the butyl group to the signal of the aromatic ring protons in the ^1H NMR spectrum in $CDCl_3$. Molecular weight as determined by gel permeation chromatography calibrated with polystyrene in THF was (2–10) × 10^4.

Grafting Reaction. The synthesis of graft copolymer 3 was carried out by the polymerization of BLA–NCA or BLG–NCA initiated by the primary amino group of 2.[8]

A THF solution of BLA–NCA or BLG–NCA (0.3–2.0 g) was mixed with a dichloromethane or THF solution (20 mL) of butyl methacrylate–1 copolymer (2) (0.5–1.0 g) at room temperature, and the mixture was stirred for 1 day. The reaction mixture was homogeneous throughout the reaction. Then the reaction mixture was poured into a large excess of cold (2–3 °C) hexane (750–1000 mL), and the precipitated polymer was filtered off and dried in vacuo. The average degree of polymerization of the poly(amino acid) chain grafted onto 2 was determined by ^1H NMR; since the content of 1 in 2 is known, the average number of amino acid residues in a side chain of the graft copolymer 3 is calculated by using the area ratio of the signal of $-COOCH_2-$ of the butyl group in the butyl methacrylate–1 copolymer backbone to that of benzyl CH_2 in the poly(β-benzyl L-aspartate) (for 3, n = 1) or poly(γ-benzyl L-glutamate) branch (for 3, n = 2).

Preparation of the Polymer Membrane. The graft copolymer dissolved in chloroform (~ 5% solution) was cast on a glass plate (5.8 cm in diameter), and evaporation was carried out in a desiccator at room temperature for 1 day. Then the membrane was dried under reduced pressure for several hours. Membranes from the copolymer having a poly(γ-benzyl L-glutamate) branch could be detached from the glass plate in water more easily than the membranes with a poly(β-benzyl L-aspartate) branch. The membranes from the latter were prepared thicker than the former and were detached carefully in tepid water. The thickness of the membranes used in the permeation experiment was about 40 and 80 μm, respectively. The membranes from these copolymers could be prepared without blending with poly(butyl methacrylate).

The membrane was fixed vertically in the center of a diaphragm-type glass cell (3 cm in diameter). In order to convert the benzyl ester group of the polypeptide branch to a carboxylate group, hydrolysis of the membrane was performed by filling both sides of the cell with 50 cm^3 of water–methanol–2-propanol (1:2:2, by volume) mixed solvent containing 0.5 wt % KOH for 16 h, followed by keeping the membrane in the fresh-mixed solvent overnight and washing 2 or 3 times. The removal of the benzyl group was confirmed by the disappearance of the infrared absorption at 700 cm^{-1} (see Figure 5). The ninhydrin test for the hydrolyzing solution after the procedure did not detect amino acid, which might have been released from the membrane by the cleavage of the polypeptide branch during hydrolysis.

Permeation. Permeation of sodium chloride was carried out as follows: Prior to the experiment, both sides of the cell were filled with an acidic (HCl) or alkaline (KOH) solution (50 cm^3) with a prescribed pH and kept for 2 days. Aqueous sodium chloride (0.1 M, 50 cm^3) was put in one side of the cell and pure water (50 cm^3) in the other. Both sides of the cell were slowly stirred at 30 °C. Small portions (1 cm^3) of the receiving side were collected after a given period of time and the concentration of sodium ion was determined by atomic absorption photometry. Percent transport was calculated without taking into account the adsorption of permeant to the membrane. Chloride ion was also found to be transported but was not measured quantitatively in the present experiment.

Permeation of styrene glycol was carried out by a similar procedure to that for sodium chloride but with a Britton–Robinson buffer solution. Prior to the experiment, both sides of the cell

Table I
Composition and Permeability of Graft Copolymer Membranes

		composition[b]			
no.	material[a]	% branching $x \approx 100$	$\overline{DP}$ of branch y	peptide content,[c] unit mol %	permeability for Na^+ after hydrolysis[d]
1	PBMA	0	0	0	no
2	PBMA-*g*-PBLA	3.5	13	32	no
3	PBMA-*g*-PBLA	10	8	47	yes
4	PBMA-*g*-PBLA	4.8	21	50	yes
5	PBMA-*g*-PBLA	10	21	70	(too brittle)
6	PBMA-*g*-PBLG	1.2	19	18	no
7	PBMA-*g*-PBLG	1.2	28	25	no
8	PBMA-*g*-PBLG	3.5	10	28	yes
9	PBMA-*g*-PBLG	12	7	45	(dispersed in water)
10	PBMA-*g*-PBLG	12	13	60	(dispersed in water)

[a] PBMA, poly(butyl methacrylate). PBMA-*g*-PBLA (**3**, $n = 1$); PBMA-*g*-PBLG, (**3**, $n = 2$). PBLA, poly(β-benzyl L-aspartate); PBLG, poly(γ-benzyl L-glutamate). [b] See structure **3**. [c] Calculated from x and y. [d] For NaCl in water.

were filled with buffer solution (50 cm^3) with a prescribed pH and kept for 2 days. Buffer solution (50 cm^3) containing styrene glycol (0.1 M) was put in one side of the cell and buffer solution (50 cm^3) in the other. The concentration of styrene glycol in the receiving side was determined by ultraviolet spectrophotometry (256 nm).

Measurements. Ultraviolet spectrophotometry was recorded on a Jasco UVIDEC-1 recording spectrophotometer using a quartz cell of 1-cm optical path length. Atomic absorption measurements were made by a Shimadzu AA-646 photometer. Infrared spectra were taken with a Hitachi 260-30 recording spectrophotometer. All spectra were measured for films cast from solution in $CHCl_3$. ^1H NMR spectra were obtained on a JEOL JNM-GX400 FT NMR spectrometer operating at 400 MHz and the deuterium of $CDCl_3$ was used as lock.

Morphology. A membrane prepared and hydrolyzed with procedures similar to those described above was immersed in 0.05 M aqueous copper(II) sulfate for 1 day. The membrane turned blue and the color could not be removed by washing with pure water, indicating the complex formation of divalent cations and carboxyl groups in the polypeptide chains.[9] The membrane, dried in vacuo, was embedded in epoxy resin and cut normal to the membrane surface into ultrathin sections (0.1 μm thick) by an ultramicrotome. The morphology of these sections was examined by a JEOL JEM-1200EX electron microscope.

Results and Discussion

Composition and Permeability of the Membrane Prepared from Polyvinyl–Polypeptide Graft Copolymers. Poly(butyl methacrylate)–poly(β-benzyl L-aspartate) and –poly(γ-benzyl L-glutamate) graft copolymers (**3**, $n = 1$ and $n = 2$) with various numbers and lengths of the polypeptide branch were synthesized. All the membranes prepared (no. 1–10) were not permeable to sodium chloride or styrene glycol before the membranes were subjected to hydrolysis. After hydrolysis, the permeability for sodium ion was examined (Table I).

As for the graft copolymers (no. 2–10), the number and the length (degree of polymerization, $\overline{DP}$) of the polypeptide branch in the graft copolymer have a remarkable effect upon the permeability to sodium ion and the mechanical strength of the membrane after the hydrolysis.

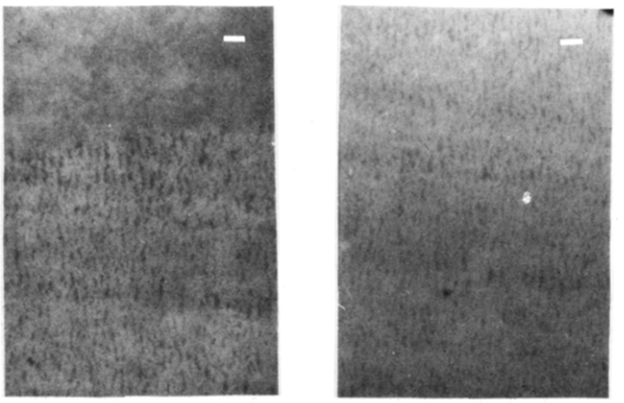


Figure 1. Transmission electron micrographs of membrane no. 4 (PBMA-*g*-PBLA; degree of branching, 4.8%; $\overline{DP}$ of branch, 21) after hydrolysis and treatment with aqueous copper(II) sulfate; bars represent 200 nm.

For membranes no. 3, 4, and 8, the permeation of sodium ion and sufficient strength were observed. Membranes with lower polypeptide contents, i.e., no. 2, 6, and 7, after hydrolysis were quite impermeable to sodium ion. On the other hand, membranes with higher polypeptide contents, i.e., no. 5, 9, and 10, were rather weak or dispersed in water after hydrolysis.

Sodium ion did not permeate through the membrane from homopolymer of butyl methacrylate (no. 1) which was subjected to the hydrolyzing conditions. The infrared spectrum of the membrane did not change before and after this treatment. Therefore, the hydrolysis of butyl ester in the backbone of the graft copolymers may be excluded under the present conditions of hydrolysis.

Block and graft copolymers are known to tend to form a microphase-separated structue in the solid state because of little or no compatibility of the different polymer segments. This is considered also the case for our membranes prepared from the polyvinyl–polypeptide graft copolymer. Figure 1 shows the transmission electron microscopic view of membrane no. 4 after hydrolysis and treatment with aqueous copper(II) sulfate. A microphase-separated structure is clearly observed: The dark, uniformly oriented stripes are considered to be copper(II) ion containing polypeptide domains, whereas the light region is the domains from poly(butyl methacrylate) chains. Any region (both inside and near the membrane surfaces) of the section showed almost the same structure as Figure 1 in terms of shape, size, and orientation of dark stripes, implying the formation of ordered microdomains over a large distance across the membrane. Although the stripes seen in Figure 1 are not always continuous, they may be considered a certain face of the continuous polypeptide domains with a cylindrical or lamellar structure, since microtoming is not necessarily done along the axis of such a structure. Incomplete staining by copper(II) ion could also be responsible for the discontinuity of the stripes.

The results described above indicate that the manifestation of the permeability in membranes no. 3, 4, and 8 was due to the formation of a transmembrane permeating pathway from the hydrophilic polypeptide domain in the stable matrix of vinyl polymer but not due to the hydrophilicity of the membrane as a whole after hydrolysis.

The morphology of the microphase-separated structure is considered to depend upon the composition of the copolymer. In the membrane with a lower polypeptide content, polypeptide segments are considered to form spherelike, discrete domains, so that hydrolysis cannot proceed in the interior of the membrane. In fact, impermeable membranes still had the infrared absorption at

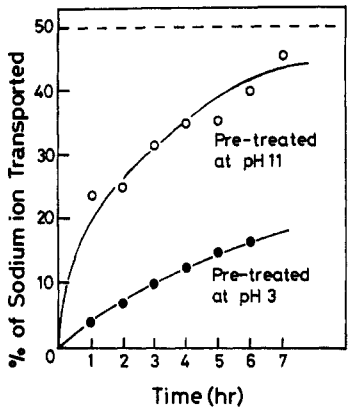


Figure 2. Time–transport curves of Na^+ in pure water (pH 7) across membrane no. 3 (PBMA-*g*-PBLA; degree of branching, 10%; $\overline{DP}$ of branch, 8) after hydrolysis and treatment with acidic (HCl) or alkaline (KOH) solution at 30 °C; initial concentration of NaCl, 0.1 M.

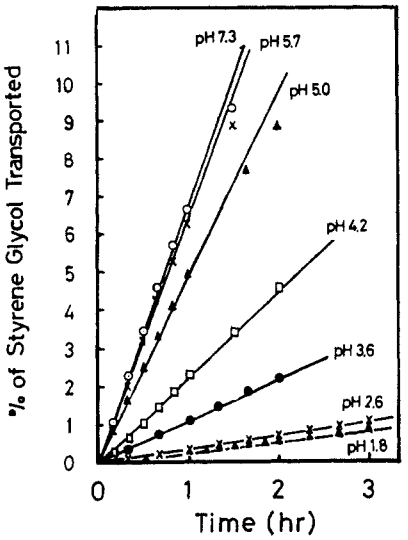


Figure 3. Time–transport curves of styrene glycol across membrane no. 4 (PBMA-*g*-PBLA; degree of branching, 4.8%, $\overline{DP}$ of branch, 21) after hydrolysis, in buffer solutions with various pH at 30 °C; initial concentration of styrene glycol, 0.1 M.

700 cm^{-1} assigned to the benzyl group to a considerable extent after treatment with the hydrolyzing solution, indicating the debenzylation was imperfect. Therefore, a continuous phase of hydrophilic polypeptide domain is not completely formed, and the permeation of sodium ion is not observed. On the contrary, in membranes having a higher polypeptide content, vinyl polymer segments are considered to a form discontinuous, spherelike microdomain and cannot play a sufficient role as a supporting matrix. The membranes were usually very fragile or dispersed in water.

The permeability to sodium ion was examined in water for a membrane after it was kept at a prescribed pH for 2 days. An example is shown in Figure 2 for the membrane prepared from a poly(butyl methacrylate)–poly(β-benzyl L-aspartate) graft copolymer (Table I, no. 3) after hydrolysis. The membrane pretreated at pH 11 exhibited a much higher permeability than that at pH 3.

pH-Dependent Permeability to Styrene Glycol. The pH-dependent permeability change was also examined for styrene glycol, a nonelectrolyte, in order to elucidate the permeability dependence upon pH independently of the direct interaction of dissociative groups of the polyelectrolyte domain in the membrane. Figure 3 illustrates the results of the experiments carried out in buffer solution

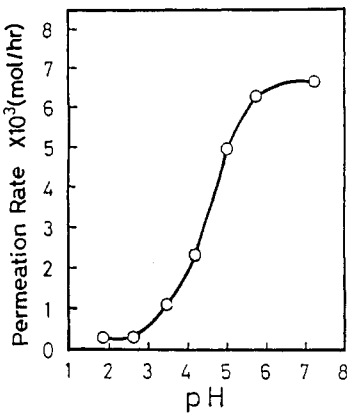


Figure 4. Rate of permeation of styrene glycol across membrane no. 4 (PBMA-*g*-PBLA; degree of branching 4.8%; $\overline{DP}$ of branch, 21) after hydrolysis, in buffer solutions with various pH at 30 °C.

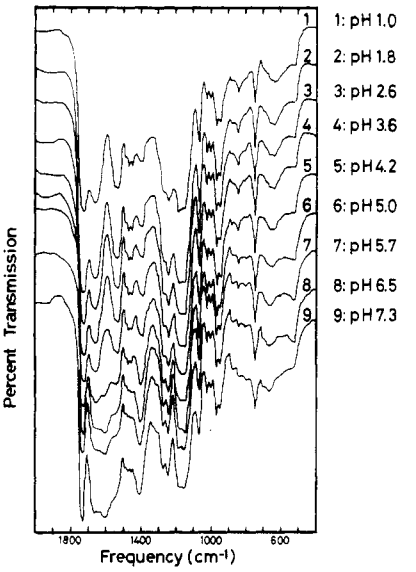


Figure 5. Infrared spectra of film from no. 4 (PBMA-*g*-PBLA; degree of branching, 4.8%; $\overline{DP}$ of branch, 21) after hydrolysis, pretreated in buffer solutions with various pH.

for the membrane prepared from a poly(butyl methacrylate)–poly(β-benzyl L-aspartate) graft copolymer (Table I, no. 4) after hydrolysis and kept in buffer solution with a prescribed pH for 2 days. From the linear part in the initial stage of the permeation, the rate of permeation was estimated as the amount of the substrate transported in a unit time (Figure 4). The sigmoidal shape of the rate–pH profile demonstrates the significant change in permeability of the membrane in the region around pH 4.5–5.

The pH-dependent permeability change of styrene glycol is considered due to the structural change of the polypeptide chain between ordered and disordered conformation brought about by the dissociation of carboxyl groups, which results in the change in hydrophilicity and mobility of the polypeptide domain. In fact, the dissociation of the carboxyl groups and the conformational change of the polypeptide chain in the membrane were observed by infrared spectral studies of the membrane (Table I, no. 4) treated previously with buffer solutions of various pH (Figure 5). In the spectrum at pH 1, the absorptions at 1660, 1540, and 630 cm^{-1} are assigned respectively to amide I, amide II, and amide V. With increasing pH the broad absorption of carboxylate group appeared at 1600 cm^{-1}. On the other hand, with an increase in pH was observed a shift of the absorption assigned to amide V from 630 to

670 cm^{-1}, which was reported to be a measure of the conformational change of poly(L-aspartic acid) chain from α-helical to random coil conformation.[10]

Thus, with a membrane from the polyvinyl–polypeptide graft copolymer, the permeability of ions as well as nonelectrolytes may be controlled over a wide range by changing pH as an external stimulation.

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Registry No. (1)·(BMA)·(BLA-NCA) (copolymer), 102493-23-2; (1)·(BMA)·(BLG-NCA) (copolymer), 102493-24-3.

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Synthesis and Properties of Carboxylated Poly(2,6-dimethyl-1,4-phenylene oxide) and Its Ionomer

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ABSTRACT: Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) has been carboxylated by using butyllithium in a mixed solvent of THF and toluene to form metalated PPO and then treating with carbon dioxide to form carboxylated PPO. A range of polymers containing from 1.5 to 41.7 mol % carboxyl groups was prepared by this reaction scheme. These carboxylic acid polymers were further reacted by esterification or metalization to form esters and sodium or cesium salts. The structure of carboxylated PPO (C-PPO) was confirmed by ^1H NMR, ^{13}C NMR, and IR spectroscopy. Glass transition temperatures, melting temperatures, decomposition temperatures, and crystallinities of C-PPO are reported. It is found that the T_g of the salt form of C-PPO increases dramatically when the carboxyl group component is more than 5.3 mol %. However, the ester form T_g shows a decrease with increasing substituent concentration. The crystallinities of C-PPO decrease as the degree of carboxylation increases. The cesium salts are the least thermally stable among those studied. Decarboxylation occurs above 350 °C for the acid form of C-PPO.

Introduction

Since the commercialization of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), a wide range of applications[1] has developed. Physical aspects of PPO such as thermodynamic properties,[2] morphologies,[3–5] thermal properties,[6] and dielectric properties[7] have been studied extensively. However, relatively few studies have been reported on the chemical modification of PPO. Hay and Chalk[8] discovered a facile method for metalating PPO under a variety of conditions, and this has led to our interest in studying the carboxylation of PPO. In the present investigation, this metalated PPO is used as a typical organometallic material for further polymer modification by a series of reactions to introduce carboxyl groups, carboxylic ester groups, and salt carboxylate groups into the PPO molecular chains. Our purpose was twofold: first, to examine the features that distinguish carboxylated PPO from unmodified PPO and second, to determine if a threshold concentration of ionic groups exists above which clusters form with resulting marked changes in properties.

In this study we have used thermal, dynamic mechanical, and wide-angle X-ray scattering (WAXS) techniques to investigate three forms of carboxylated PPO: acid, ester, and salt. These three functional groups are located in pendant positions on the PPO methyl groups.

The results of thermal and dynamic mechanical studies demonstrate that the nature of these pendant groups plays an important role in determining the glass transition temperatures of these materials. Moreover, the WAXS data demonstrate that the concentration of ionic groups affects the degree of crystallinity. At low levels of carboxylation, the materials behave in general very much like PPO but this behavior is modified significantly as the level of carboxylation is increased. Evidence is presented for the existence of ionic clusters by means of thermal analysis. We have found a critical ion concentration (5.3 mol %) above which clusters may exist. At high carboxylation levels (above 17 mol %) their salt forms display a significantly broadened T_g.

Experimental Section

Materials. The starting PPO was purchased from Aldrich Chemical Co. It was used as received without further purification other than drying at 100 °C for 24 h in a vacuum oven prior to use. The molecular weight was measured by GPC (M_n = 29 244; M_w = 67 559).

Tetrahydrofuran was refluxed over calcium hydride for 2 days and then distilled to remove water, peroxide inhibitor, and other impurities. Toluene was refluxed over phosphorus pentoxide and was distilled.

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