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Synthesis, characterization and investigation of dielectric properties of two-armed graft copolymers prepared with methyl methacrylate and styrene onto PVC using atom transfer radical polymerization

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Poly(vinyl chloride-*co*-vinyl diethanolamine) copolymers were synthesized by modification of PVC with diethanolamine. Acylation of —OH groups in the copolymer with α-bromoisobutirylbromide gave poly{-vinyl chloride-*co*-vinyl-bis[2-(2-bromo-2-methylpropanoato)ethyl]amine} as two-armed macroinitiator. A series of grafting studies with methyl methacrylate and styrene was carried out in the presence of the macroinitiator and the catalyst CuBr/2,2′-bipyridyl (bpy) at 110 °C. FT-IR Spectra of all the polymers were recorded for the structural characterization, and ^{1}H and ^{13}C NMR spectra were also used in the characterization PVC-*graft*-methyl methacrylate. During the grafting reaction at 110 °C, the number-average molecular weight of the macroinitiator increased from 63,700 (polydispersity 2.17) to 159,000 (polydispersity 1.40) at 20 h in case of methyl methacrylate, and to 86,900 (polydispersity 1.70) at 48 h in case of styrene. The thermally stability of PVC modified with diethanol amine and the macroinitiator was similar that of PVC as initial decomposition temperature, but the graft copolymers showed higher thermal stability than PVC. While the glass-transition temperatures of PVC, PVC modified with diethanol amine and the macroinitiator showed a glass-transition temperature at around 91 °C, the graft copolymers of methyl methacrylate and styrene showed at 120 °C and 98 °C, respectively. The dielectric features of the macroinitiator and the graft copolymers against the frequency at the room temperature were examined. Dielectric constant of macroinitiator was calculated as 4.76 at 100 Hz. Dielectric features of the polymers against the temperature at three different frequency was examined.

1. Introduction

Poly(vinyl chloride) (PVC) is one of the most important commercial polymers due to its low production costs and its excellent stability to acids and bases and also PVC is well known for its compatibility with additives including plasticizers, heat stabilizers, lubricants, fillers, and other polymers which enable it to have a variety of mechanical properties [1].

Modification of PVC can generally be achieved by nucleophilic substitution reactions of chlorine atoms as an appropriate method of improving properties [2]. Modifications of PVC with many nucleophiles, such as I^-, SCN^-, OH^-, N_3^- and phthalimide anion [3], pyrazole, 3,5-dimethylpyrazole and 2-mercaptobenzimidazole [4], 1,4-phenylenediamine [5], ethylenediamine [6], potassium ethyl xanthogenate [7], amino thiophenol [8], were studied.

Several synthetic methods for grafting of PVC have been reported by radical chain transfer reaction, such as in grafting of PVC with glycidyl methacrylate [9], methyl methacrylate [10] and butyl acrylate [11], by ionic polymerization from labile chlorine in PVC, such as in the grafting with isobutylene [12], by aid of polyperoxy radical [13], and by aid of electrochemical polymerization [5] in the grafting with aniline. Grafting of styrene and various acrylates was achieved by ATRP with the chloroacetyl group introducing to the polymer as initiating sites [14]. Percec and Asgarzadeh [15,16] and Bıcak and Özlem [17], and Chen and coworkers [18] reported the utility of ATRP in the grafting of some vinyl monomers by initiation via the labile chlorines of PVC.

In this study, we report the synthesis of poly(vinyl chloride-*co*-vinyl diethanolamine), PVC-DEA, from modification of PVC with diethanolamine, synthesis of the macroinitiator, poly[vinyl chloride-*co*-bis(2-bromo-2-methylpropanoatoethyl)amino vinyl], PVC-DEAB, preparing the graft copolymers poly(vinyl chloride-g-methyl methacrylate), PVC-g-PMMA, and poly(vinyl chloride-g-styrene), PVC-g-PSt via atom transfer radical polymerization (ATRP). Structural, thermal and molecular weight characterizations of all the polymers were given. Dielectric properties of PVC, PVC-DEA, PVC-DEAB and PVC-g-PMMA were investigated as function of temperature and frequency.

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2. Experimental section

2.1. Materials

Methyl methacrylate (MMA) and Styrene (Aldrich) were distilled under vacuum before use. CuBr, 2,2′bipyridyl (bpy), diphenyl ether, diethanolamine, α-bromoisobutyryl bromide, tetrahydrofuran (THF), N,N-dimethylformamide (DMF), and ethanol (Fluka) were used without further purification. PVC was obtained from a local company named Keban Plastic Co (M_n = 67000, M_w/M_n = 1.85).

2.2. Modification of poly(vinyl chloride) with diethanolamine

Modification of PVC with diethanolamine was carried out according to the method adapted from the literature [19]. 10 g (160 mmol) of the PVC was placed in a 50 mL flask, dissolved in 20 mL of THF, and diluted with 30 mL of DMF. Diethanolamine (0.686 g, 6.5 mmol) and $NaHCO_3$ (0.27 g, 3.3 mmol) was added to the copolymer solution. The mixture was stirred and heated for 24 h at 90 °C under argon. The reaction mixture was cooled to room temperature, filtered off, and the resulting product, PVC-DEA, was precipitated into excess ethanol and purified from the THF solution by reprecipitating in ethanol.

2.3. Synthesis of the macroinitiator

Ten grams (3.13 mmol) of PVC-DEA was dissolved in dry THF (20 mL) and triethylamine (0.63 g, 6.3 mmol) was added. After cooling to 5–6 °C, a solution (2 mL) of dry THF containing α-bromoisobutyryl bromide (1.44 g, 6.3 mmol) was added gradually over 15 min. After stirring overnight at room temperature, the precipitate was filtered off and the acylated copolymer (the macroinitiator), PVC-DEAB, was precipitated with excess ethanol. The copolymer was filtered and dried, dissolved in THF, and reprecipitated into ethanol. Then, the copolymer was dried under vacuum at 40 °C for 24 h.

2.4. Synthesis of graft copolymers by atom transfer radical polymerization

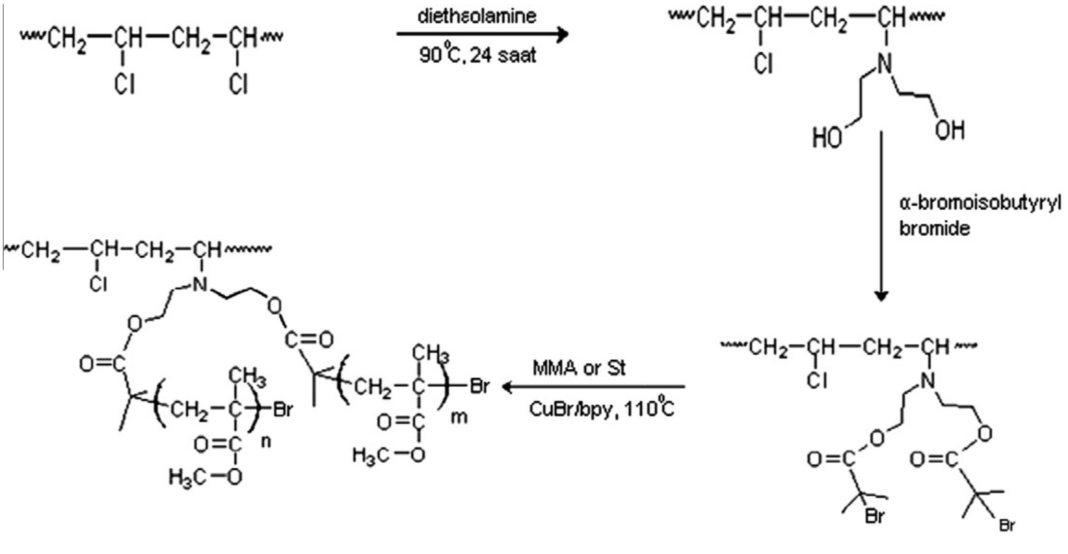
Atom transfer radical copolymerizations were carried out in a 25 mL flask equipped with a condenser. The necessary amount of the macroinitiator PVC-DEAB was dissolved in dry THF (1 mL per 0.1 g of macroinitiator), and the following were then added to the solution: the appropriate monomer (methyl methacrylate or styrene), macroinitiator, CuBr, and 2,2′-bipyridyl at a mol ratio of 200:1:2:4, respectively. The solution contains the same molar amounts of α-bromoisobutyroxy group and CuBr. Argon gas was passed through the solution for 15 min. The polymerization flask was allowed to react at 110 °C for the desired time, and then the graft copolymer was precipitated into slightly acidic ethanol. The graft copolymers, poly(vinyl chloride-*g*-methyl methacrylate), PVC-*g*-PMMA, and poly(vinyl chloride-*g*-styrene), PVC-*g*-PSt, was purified from THF solution by reprecipitating with slightly acidic ethanol.

2.5. Instrumentation

^{1}H NMR spectra were obtained on a 400 MHz Bruker AVIII 400 machine, using $CDCl_3$ as the solvent, and tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin–Elmer Spectrum One FTIR spectrometer. Calorimetric measurements were carried out on a Shimadzu DSC-50 thermal analyzer under N_2 flow a using a heating rate of 20 °C/min. Thermal stability studies were carried out on a Shimadzu TGA-50 thermobalance under N_2 flow with a heating rate of 10 °C/min. The molecular weight and molecular weight distribution were determined using an Agilent 1100 gel permeation chromatography (GPC) system equipped with a Waters Styragel column, a refractive index detector and a pump. The column was calibrated with polystyrene, and samples were eluted using THF.

2.6. Capacitance measurements

The polymer was ground with an agate mortar and pestle, and the final fine powder was pressed at four tons of pressure into disk-shaped samples with a thickness ranging from 0.94 mm to 2.22 mm and a diameter of 12 mm. The entire surface of the discs was coated with silver paste, which acts as a good contact for capacitance measurements. The capacitance measurements were carried out at room temperature with a QuadTech 7600 precision LRC meter impedance analyzer over the frequency range 40 Hz–2 kHz. The dielectric features against the frequency of PVC, PVC-DEA, PVC-DEAB and PVC-*g*-PMMA at room temperature were examined, and dielectric features of the polymers against the temperature were examined.



Scheme 1. Synthesis of two-armed graft copolymer.