

Preparation of Copolymers by Controlled Radical Polymerization and their Applications

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Introduction

In the last 2 decades, new radical polymerization techniques were developed that make it possible to synthesize polymers with controlled architectures and properties. Typical representatives of these procedures are the iniferter technique, stable free radical polymerization, atom transfer radical polymerization, and, quite recently, radical polymerization with reversible addition and fragmentation chain transfer. Each of these methods had its specificity, its advantages and drawbacks. However, one feature is common for all of them. The control of the polymerization is achieved by reversible end-capping of growing polymer chains. At higher temperatures, usually above 100 °C, the reversibly terminated, i.e., potentially active chains undergo thermal homolysis.

A widely studied approach to the radical pseudo-living polymerization involves the use of stable nitroxide free radicals, such as TEMPO. Nitroxide-based systems for the controlled polymerization have some important advantages: (a) nitroxyl radicals do not initiate, they only terminate, thus enhancing the possibility to obtain polymers of a narrow molecular weight distribution; (b) a relatively labile bond between the chain and the terminal nitroxyl group is favorable to the polymerization process; (c) the absence of an added metal complex, which is a necessary component of an initiating system in atom transfer radical polymerization, results in tolerance to the presence of functional groups and easy purification of products.

Originally, the nitroxide-mediated radical polymerization (NMP) has been successfully applied to styrene, its derivatives, and comonomers, 2- and 4-vinylpyridines are attractive compounds. Nowadays, many researcher paid attention to the application of the products from living radical polymerization. One of them is the field of surface medication of nanoparticles used as functional nano-fillers.

Surface modification of clay minerals has become increasingly important for improving the practical applications of clays such as polymeric nanocomposites. Commercially available organophilic layered silicates (OLS) with alkyl chain modifier have critical problems that the aliphatic components limit the thermal stability as well as compatibility with polymer matrix. In the view point of thermal stability, the processing temperature of most of polymers is high enough to degrade the alkyl modifiers of layered silicates, which imply that the commercially available OLSs are not suitable for the preparation of polymeric nanocomposites. And also, to enhance the compatibility between OLS and polymer matrix, the well-structured organic modifiers that impart compatibility to specified polymer matrix are needed. To solve these problems, we used the copolymer modifiers having phenyl components, and successfully developed a route for the preparation of amine functionalized polymer based on oligostyrene and its block copolymers.

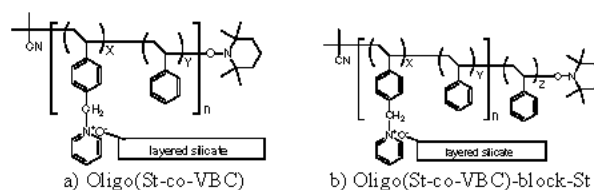
Experimental

Materials and Measurements. Styrene was purchased from Aldrich Chemical Company. Inhibitor was removed by extraction several times. After that, styrene was purified by distillation under reduced pressure at 40 °C. 4-Vinylbenzyl chloride (VBC) containing 500ppm 4-tert-butylcatechol and 500ppm nitroparaffin inhibitors were also purchased from Aldrich Co. For purification of VBC, 4-tert-butylcatechol and nitroparaffin were removed by disposable prepacked columns as inhibitor remover. The free radical inhibitor, 2,2-azobis-isobutyronitrile (AIBN), was obtained from Dupont and purified by recrystallization twice from methanol. 2,2,6,6-Tetramethylpiperidin-1-oxyl (TEMPO, Aldrich) was used as received. The one of source clays, sodium montmorillonite (Na-MMT) in a type of smectite with a cationic exchange capacity (CEC) of 157mequiv/100g, was provided by Southern Clay Product Co. (USA). ¹H-NMR spectra were recorded on Bruker AMX-300MHz spectrometer. FT-IR spectra were determined by Bio-Rad Digilab Division FTS-165 spectrometer. The conversion of the monomers

were calculated from the GC (HP 5880A). Molecular weight and polydispersity index of the copolymers were determined by GPC. Energy dispersive spectrometer (EDS) spectra were obtained from phoenix (EDS model) provided by EDAX Co. X-ray diffraction (XRD) was characterized by D8-Discover XRD with GADDS (Bruker) attached CuK α radiation ($\lambda=1.5405\text{nm}$) and X-ray diffractometer (40kV, 40mA) from 1.5 to 10 $^\circ$ at a scanning rate of 1 $^\circ$ /min. Transmission electron microscopy (TEM) was obtained from Hitachi H-7600. Thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) were carried out on TA Instruments TGA Q500 and DSC Q1000 at a heating rate of 10 $^\circ$ C/min under nitrogen flow, respectively.

Copolymerization. In a typical run, 0.23g (1.43mmol) of AIBN, 0.54g (3.4mmol) of TEMPO, 45.45g of Styrene (0.44mmol) and 3.89g (0.11mmol) of VBC were introduced in a Schlenk flask. After three freeze-thaw-pump cycles, the reactor was immersed in an oil bath at 135 $^\circ$ C. After the required duration, the reaction was stopped by cooling the flask. The resulting oligo(St-co-VBC) was recovered by precipitation in methanol and dried at room temperature under reduced pressure. By controlling the reaction time, we have synthesized that molecular weight of oligo(St-co-VBC) confirmed via GPC was around 9,700–25,500. The reactive ratio of styrene and VBC was calculated from the intensity of the signal of the vinylic protons corresponding to the residual VBC in comparison with the intensity of the signal for the benzylic protons through the ¹H-NMR. And also, we synthesized block copolymers from oligo(St-co-VBC) which molecular weight is 7,000g/mol.

Amination reaction. Oligo(St-co-VBC) containing onium salt content were prepared by reaction of oligo(St-co-VBC) and pyridine in toluene at 70 $^\circ$ C for 12hr under nitrogen environment as shown in **Scheme 1**. The resulting onium salt of oligo(St-co-VBC) was recovered by precipitation in methanol and dried at room temperature under reduced pressure.



Scheme 1. Chemical structures and schematic drawings of organophilic layered silicates

Synthesis of OLS. In the m-aA case, the dispersion of Na-MMT (3.043g of Na-MMT + 57.817g of distilled water) was added to the solution of oligo(St-co-VBC) containing ammonium salt (4.257g), and this mixture was stirred vigorously at 70 $^\circ$ C for 24hr with a gradual addition of DMF (390g). The ionic exchange reaction between the onium salt of oligo(St-co-VBC) and the sodium ions in the layered Na-MMT is a main driving force for the Na-MMT intercalation. A white precipitate was isolated centrifugation to separate the OLS from co-solvent of distilled water and DMF. The resulting OLS was washed centrifugally with deionized water several times. After that, the product was freeze-dried for 48hr. The dried cake was ground and screened with a 325mesh sieve.

Results and discussion

We synthesized series of oligo(St-co-VBC) and oligo(St-co-VBC)-block-styrene via NMP and performed further research their potential application to the organic modifier of layered silicate such as MMT. After preparation of several kinds of oligomers, the relative ratio and content of styrene and functional VBC were determined by gas chromatography and ¹H-NMR. We successfully controlled the fraction of VBC to prepare the resulting copolymers and block copolymers. The content of chloromethyl group was determined by ¹H-NMR. And also, the reaction conditions, molecular weight, PDI and inherent viscosities were listed in **Table 1**.

Table 1. Content of functional group and M_n of oligomers.

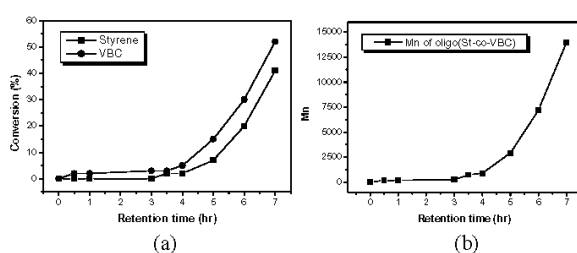
| Code | Relative ratio (St : VBC) | | M_n^a (g/mol) | PDI ^b | IV ^c (dL/g) |
|------|------------------------------|--------|--------------------|------------------|---------------------------|
| | by GC | by NMR | | | |
| A | 77:23 | 77:23 | 9,700 | 1.26 | 0.087 |
| B | 75:25 | 77:23 | 14,200 | 1.26 | 0.098 |
| C | 75:25 | 78:22 | 19,500 | 1.31 | 0.125 |
| D | 76:24 | 75:25 | 25,500 | 1.42 | 0.156 |

a) Measured by GPC

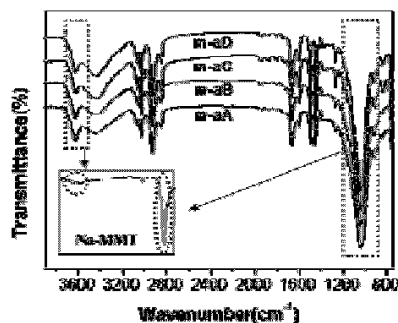
b) PDI: Polydispersity Index(M_w/M_n)

c) IV: Inherent Viscosity; measured in DMAc, 0.5g/dL at 25 °C

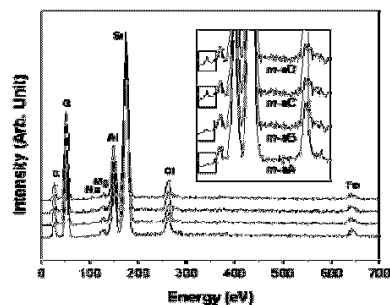
The NMP method gives narrow molecular weight distribution as compared to that of free radical polymerization. Furthermore, we have confirmed that the oligo(St-co-VBC)s prepared by NMP were excellent modifier below the molecular weight 15,000 g/mol. The conversion and number average molecular weight were shown in Figure 1. From these result, we can easily control the molecular weight by adjusting the reaction time.

**Figure 1.** Conversion and molecular weight of oligo(St-co-VBC) according to the reaction time.

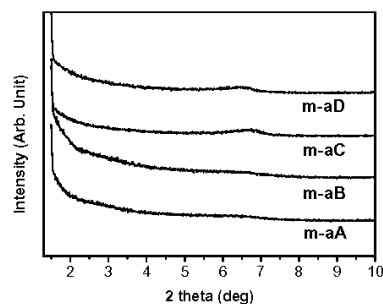
The ionic exchange reaction between the pendent onium salt of oligomers was carried out, after the quantitative amination reaction with pyridine. In this reaction, the sodium ions exist in the layered Na-MMT is exchanged with pendent onium ion of oligomers. And also during the process, NaCl is generated and diffused away from the swelled clay in water. The chemical structures of organophilic layered silicates were confirmed by assigning of the absorption from 3600 and 1050 cm^{-1} of MMT and the other characteristic bands of polystyrene as shown in Figure 2. In addition, AAS analysis showed that the displacement ratio of Na is above 99% in the cases of using A and B, this means that the copolymers are coexist with MMT; i. e., the synthesis of organophilic layered silicates was successful.

**Figure 2.** FT-IR spectra of organophilic layered silicates.

To identify the molecular weight effect on the ion-exchange reaction, EDS spectra were taken as shown in Figure 3. In these spectra, the higher molecular weight of modifiers, the smaller displacement ratio, this is because that the smaller molecular weight of modifier can easily diffuse into the interlayer of layered silicate in homogeneous and aqueous solvent. On the other hand, C and D materials were precipitated during the ion-exchange reaction to incomplete products.

**Figure 3.** EDS spectra of organophilic layered silicates.

The internal structure was examined by wide angle X-ray diffraction (WAXD) and reproduced in Figure 4. No WAXD peaks are observed between $2\theta=2^\circ$ and 10° for OLS, indicating the gallery spacing of the OLS is greater than the size of silicate itself.

**Figure 4.** XRD diffractograms of organophilic layered silicates

Conclusions

The oligo(St-co-VBC)s with controlled molecular weight were synthesized via nitroxide mediated polymerization method. The functional chloromethyl groups are quantitatively converted into onium group which is capable to exchange the sodium ion on the surface of layered silicate such as MMT. We also successfully prepared organophilic layered silicates whose surface is covered with styrenic copolymers. The chemical structure of OLS was confirmed by spectroscopic means such as FT-IR and EDS and their internal structure was investigated by XRD and TEM. These kind of analysis showed that copolymers were very effective organic modifiers to change the surface characteristics of layered silicates.

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