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Synthesis and characterization of polyacrylonitrile grafted with poly(2,6-dimethyl-1,4-phenylene oxide)

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SUMMARY

Free radical copolymerization of acrylonitrile (AN, M_1) with poly(2,6-dimethyl-1,4-phenylene oxide)-ω-vinylbenzyl ether (PPO-VBE, M_2, $\overline{M}_n$ = 4200 g/mol, $\overline{M}_w/\overline{M}_n$ = 1.04) was performed at 60 °C in either a mixture of N,N-dimethylformamide/toluene or tetrahydrofuran, using 2,2'-azoisobutyronitrile (AIBN) as initiator. The characterization of the resulting polyacrylonitrile grafted with poly(2,6-dimethyl-1,4-phenylene oxide) (PAN-g-PPO) was performed by 200 MHz ^{1}H-NMR spectroscopy and solubility.

INTRODUCTION

The copolymerization of a macromonomer of narrow molecular weight distribution with a low molecular weight monomer represents the "state-of-the-art" approach to the synthesis of graft copolymers of well-defined architecture.[1-3] However, the copolymer composition and the sequence distribution of the resulting graft copolymer is determined by both the monomer/macromonomer molar ratio and the reactivity ratios of the comonomers. Previous results from our laboratory have demonstrated that the determined "reactivity" of poly(2,6-dimethyl-1,4-phenylene oxide)-ω-vinylbenzyl ether (PPO-VBE) is influenced by the molecular weight of the macromonomer,[4] by the total monomer concentration,[5,6] and by the nature of the polymerization solvent.[5] The dependence of macromonomer reactivity, determined from copolymerization experiments with methyl methacrylate (MMA) and butyl methacrylate (BMA), on the total monomer concentration and on the polymerization solvent was interpreted based on a micelle formation model, in which the comonomer concentrations are partitioned between the bulk of free solvent and around the growing chain. The determined reactivity ratio (r_1) was rationalized as a product of the partition coefficient, k, and the real reactivity ratio, r_1^o. This explanation assumes that the r_1^o is constant for the copolymerization of PPO-VBE with MMA and BMA and the non-

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*To whom offprint requests should be sent ideality of polymerization medium influences the value of *k* . It has also been shown that most of the resulting graft copolymers have in fact a structure like AB diblock copolymers.[5] Therefore, these graft copolymers are of interest as polymer emusifiers for immiscible blends.[7]

This communication describes the free radical copolymerization of PPO-VBE macromonomer with acrylonitrile and the characterization of the resulting polyacrylonitrile grafted with poly(2,6-dimethyl-1,4-phenylene oxide).

EXPERIMENTAL

Materials

Acrylonitrile (Aldrich) was freshly distilled under nitrogen. 2,2'-Azobisisobutyronitrile (AIBN, Fluka) was freshly recrystallized from methanol below 40 °C. Toluene was washed with dilute sulfuric acid to remove thiophene and/or olefins, then with water, dried over anhydrous calcium chloride, and distilled from sodium. Tetrahydofuran (THF) was distilled from lithium aluminum hydride. N,N-dimethylformamide (DMF) was distilled from barium oxide.

Techniques

200 MHz ^{1}H-NMR spectra were recorded on a Varian XL-200 spectrometer. All spectra were obtained at 100 °C in dimethyl sulfoxide (DMSO)-d_6 with TMS as internal standard. The determination of molecular weight of the PPO-VBE macromonomer was performed as previously described.[5]

Synthesis of PPO-VBE Macromonomer

PPO-VBE macromonomer was synthesized by a phase transfer catalyzed etherification of ω-2,6-dimethylphenol-poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-OH) with vinylbenzyl chloride.[4] PPO-OH was synthesized by the phase transfer catalyzed polymerization of 4-bromo-2,6-dimethylphenol.[8] PPO-VBE macromonomer was fractionated by precipitating the chloroform solution with methanol as previously described.[4,5] The PPO-VBE macromonomer used in this study has $\overline{M}_n = 4200$ g/mol, $\overline{M}_w/\overline{M}_n = 1.04$.

Free Radical Copolymerization of Acrylonitrile with PPO-VBE Macromonomer

The copolymerization experiments were performed either in a mixture of DMF and toluene or in THF. The detailed copolymerization compositions are listed in Table I. An example for the copolymerization and polymer purification is given below.

PPO-VBE (0.112 g) was dissolved in 4.356 g toluene in a polymerization tube.[4] After the complete dissolution, 6.357 g DMF, 1.167 g acrylonitrile and 0.056 g AIBN were introduced. The tube was sealed and degassed by four freeze-thaw cycles on a vacuum line. The tube was subsequently filled with dry high purity nitrogen and heated in an oil bath at 60 °C. During the polymerization a precipiate was formed in the polymerization tube. The polymerization was continued for 43 h. The content was precipitated into methanol, the filtered precipitate was repeatedly washed with toluene to remove the unreacted PPO-VBE macromonomer. The resulting precipitate was dried in vacuo. The dried precipitate was dissolved in DMF and precipitated in methanol. The precipitate was dried in vacuo to yield 0.796 g (62%) polymer.

Table I. Synthesis of Polyacrylonitrile-g-Poly(2,6-dimethyl-1,4-Phenylene Oxide) (PAN-g-PPO) by Free Radical Copolymerization of Acrylonitrile (M_1) with PPO-VBE (M_2, $\overline{M}_n$ = 4200 g/mol, $\overline{M}_w/\overline{M}_n$ = 1.04). Polymerization Temperature, 60 °C. Initiator, AIBN.

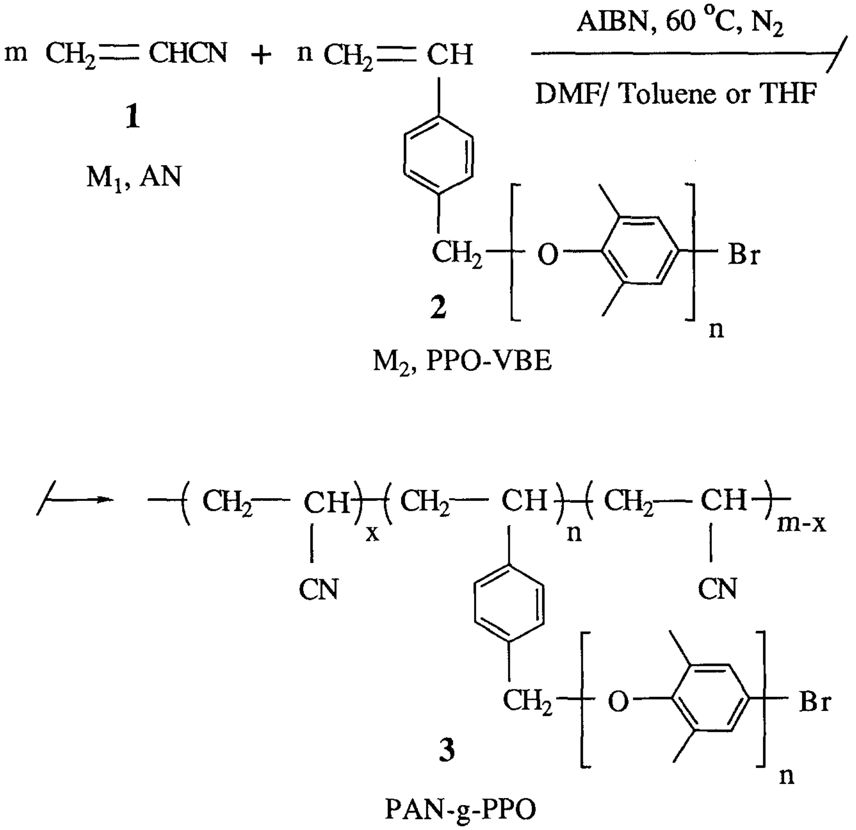
Experiment No.	M_1 (g)	M_2 (g)	AIBN (g)	Solvent (g)	Feed $[M_1]_o/[M_2]_o$	Polymerization Time (h)	Polymer Yield (%)
1	1.167	0.113	0.056	DMF(6.375)+ Toluene(4.350)	815	43	62
2	0.947	0.106	0.056	THF(5.278)	705	17	66

RESULTS AND DISCUSSION

The free radical copolymerization of acrylonitrile (M_1, AN) and PPO-VBE (M_2) is shown in Scheme I. The copolymerization experiments were performed at 60 °C, under N_2 using AIBN as a free radical initiator. The conditions and the results of the copolymerization experiments are listed in Table I.

Due to the difference in the solubilities of polyacrylonitrile (PAN) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), a mixture of DMF and toluene was used in Experiment No. 1 (Table I) since DMF and toluene are good solvents for PAN and PPO respectively. Even though the polymerization was homogeneous in the early stage of the reaction, after a short time the polymerization mixture becomes heterogeneous. The polymerization resulted in a 62% yield of copolymer. Experiment No. 2 was performed in THF leading to 66% yield of copolymer.

The resulting reaction mixture was first precipitated in methanol and the precipitate was washed with toluene to remove any residual unreacted PPO-VBE macromonomer present in the copolymer sample.



Scheme I. Synthesis of polyacrylonitrile-g-PPO (PAN-g-PPO) by free radical copolymerization of acrylonitrile (M_1) and PPO-VBE (M_2).

The 200 MHz ^{1}H-NMR spectrum (DMSO-d_6, 100 °C, TMS) of PAN-g-PPO (Sample from Exp. No. 1) is presented in Figure 1. The resonances due to the methylene and methine groups of the polyacrylonitrile main chain are observed at 2.08 and 3.15 ppm. The resonance due to the methyl groups on the PPO grafts is observed as a shoulder at 2.13 ppm, the corresponding aromatic resonance is observed at 6.49 ppm. Therefore, the resulting polymer is a graft copolymer with polyacrylonitrile as the main chain and with PPO as the side chain grafts as shown in Scheme I. The weight percentages of PPO in the initial reactions mixtures are 8.8% and 10.1% for Exp. No.1 and No. 2 respectively. However, the corresponding graft copolymers contains 5.7% and 6.1% of PPO by weight as determined from the ^{1}H-NMR spectra. Therefore, the graft copolymers contains only 60-65% of the PPO in the initial monomer mixtures. The decrease in the PPO content

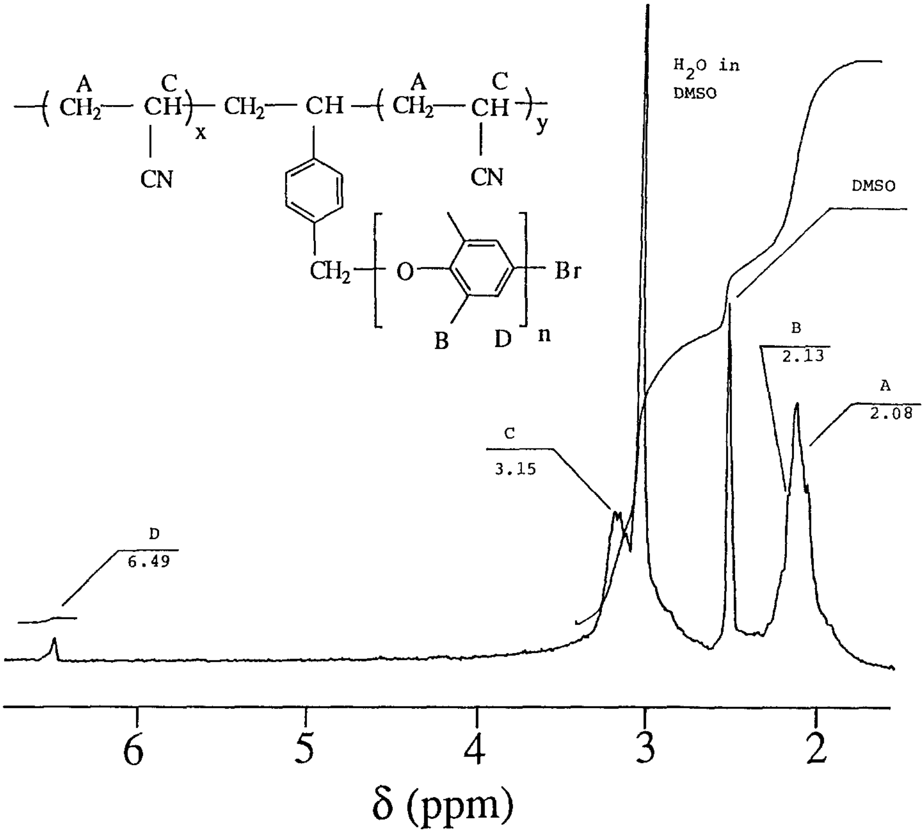


Figure 1. 200 MHz ^{1}H-NMR spectrum (DMSO-d_6, 100 ^{o}C, TMS) of the PAN-g-PPO (Sample No. 1, Table I).

is caused by the precipitation of the copolymer from the reaction mixture. Since PPO-VBE is soluble in the reaction medium, it can not be incorporated into copolymer once the copolymer precipitated out of the solution.

The resulted graft copolymers are soluble in DMSO and DMF which are good solvents for PAN, but they are not soluble in toluene, benzene and chloroform which are good solvents for PPO. The addition of toluene to the DMSO solution of the resulting graft copolymer causes turbidity. However, a transparent film was cast from the DMSO solution of the graft copolymers. These observations indicate the existence of a graft copolymer which is most probably microphase separated but gives rise to very small domain size.

As indicated in Table I, these copolymerizations were performed at $[M_1]/[M_2]$ molar ratios of 705 and 815 . Therefore the sequence length of polyacrylonitrile, $\bar{n}_1 >> 1$. As discussed previously[5] this leads to a copolymer which has a structure analogous to an AB type diblock copolymer of polyacrylonitrile and PPO.

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