Macromolecules **2002,** *35,* 1146−1148

Synthesis of Hyperbranched Polyacrylates in Emulsion by Atom Transfer Radical Polymerization

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Received August 15, 2001

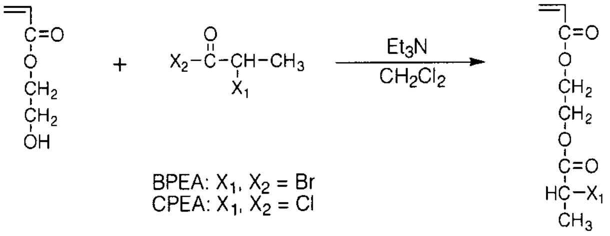
Introduction. Our effort to prepare hyperbranched polymers by atom transfer radical polymerization (ATRP) in emulsion was motivated by the need to enhance the molecular weight of the polymers. Although ATRP has been successfully applied to the preparation of hyperbranched polymers,[1−3] a molecular weight on the level of linear polymers has hardly been achieved in the bulk or solution polymerization. One of the advantages of emulsion polymerization is being able to attain both high molecular weight and high reaction rate simultaneously.

As ATRP is more tolerant to the presence of water and other contaminants than ionic living polymerization systems are,[4] recent efforts have been successfully expended in extending ATRP to water-borne systems.[5−7] However, as far as we know, no attempt to prepare a hyperbranched polymer using ATRP in emulsion has been reported. We report here on the first attempt to synthesize hyperbranched polymers by copper-mediated ATRP of 2-(2-bromopropionyloxy)ethyl acrylate (BPEA) and 2-(2-chloropropionyloxy)ethyl acrylate (CPEA) in emulsion.

Experimental Section. BPEA was synthesized according to Matyjaszewski et al.,[3] except that triethylamine was used in place of pyridine and that the final purification was by column chromatography. A silica gel (Merck Kieselgel 60 (70−230 mesh)) column with ethyl acetate/*n*-hexane (1/6 v/v) was used. CPEA was prepared through the identical procedure using 2-chloropropionyl chloride (9.6 mL, 99.0 mmol) as the acid halide (see Scheme 1). CPEA: ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.44 (dd, $J = 1.5, 17.2$ Hz, 1H), 6.14 (dd, $J = 10.4, 17.2$ Hz, 1H), 5.88 (dd, $J = 1.5, 10.4$ Hz, 1H), 4.42 (m, 5H), 1.70 (d, $J = 7.0$ Hz, 3H).

4,4′-Dipropyl-2,2′-dipyridyl (DPrD), 4,4′-dipentyl-2,2′-dipyridyl (DPeD), and 4,4′-dinonyl-2,2′-dipyridyl (DNoD) were prepared from 4,4′-dimethyl-2,2′-dipyridyl (DMeD, 0.442 g, 2.4 mmol) following the method of Torki et al.[8] Bromoethane (0.45 mL, 6.0 mmol), 1-bromobutane (0.64 mL, 6.0 mmol), and 1-bromooctane (1.04 mL, 6.0 mmol) were used as the alkyl bromides. DPrD: ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.56 (d, $J = 5.0$ Hz, 2H), 8.23 (d, $J = 1.6$ Hz, 2H), 7.12 (dd, $J = 1.6, 5.0$ Hz, 2H), 2.67 (t, $J = 7.5$ Hz, 4H), 1.72 (m, 4H), 0.96 (t, $J = 7.5$ Hz, 6H). DPeD: ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.56 (d, $J = 5.0$ Hz, 2H), 8.23 (d, $J = 1.6$ Hz, 2H), 7.13 (dd, $J = 1.6, 5.0$ Hz, 2H), 2.69 (t, $J = 7.5$ Hz, 4H), 1.69 (qn, $J = 7.5$ Hz, 4H), 1.34 (m, 8H), 0.89 (t, $J = 6.9$ Hz, 6H). DNoD: ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.56 (d, $J = 5.0$ Hz, 2H), 8.23 (d, $J = 1.6$ Hz, 2H), 7.13 (dd, $J = 1.6, 5.0$ Hz, 2H), 2.69 (t, $J = 7.5$ Hz, 4H), 1.69 (qn, $J = 7.5$ Hz, 4H), 1.29 (m, 24H), 0.87 (t, $J = 6.7$ Hz, 6H).

Scheme 1



For the emulsion polymerization, a two-necked flask equipped with a reflux condenser was charged with copper(I) bromide (3.3 mg, 0.023 mmol), the ligand (0.046 mmol), and a nonionic surfactant, Brij 98 (0.4 g). The flask was sealed with a rubber septum, and the BPEA (11.4 mmol) or CPEA (11.3 mmol) degassed by nitrogen bubbling was added via a syringe under vacuum. The vacuum−nitrogen cycle was repeated three times to remove any oxygen, and then degassed deionized water (10 mL) was added via a syringe. Immediately after mixing, the flask was placed in an oil bath kept at a given reaction temperature. The samples for studying the rate of polymerization were taken under a nitrogen atmosphere at given time intervals. The polymerization was terminated by cooling the reaction mixture to the ice bath temperature, followed by exposing to the air. After water was evaporated, the mixture was diluted with THF. Addition of the polymer solution to a large excess of methanol resulted in the polymer precipitate, which was subsequently dried overnight under high vacuum at 60 °C. Conversion of the double bonds was determined using ^{1}H NMR spectroscopy. The molecular weight and molecular weight distribution were measured using gel permeation chromatography at 35 °C on three polystyrene gel columns that were connected to a Viscotek LR125 laser refractometer. THF was used as the eluting solvent at a flow rate of 1.0 mL/min, and the molecular weight calibration curve was determined using polystyrene standards.

Results and Discussion. Table 1 shows the experimental conditions and results of the polymerizations. The emulsion polymerizations of BPEA with bipyridine (Bpy) were so fast that gelation was observed to occur, and the cross-linked polymer precipitated. This was also the case in the polymerization of CPEA. This lack of control in the reaction was attributed to the poor solubility of CuBr$_2$/Bpy in the organic phase.[9−12] When, in the equilibrium reaction of $\mathrm{R{-}X} + \mathrm{Cu(I)} \rightleftharpoons \mathrm{R}^\bullet + \mathrm{X{-}Cu(II)}$, active radicals could not be rapidly deactivated to become dormant species, the excessively high concentration of radicals drove the polymerization very fast and, subsequently, to the coupling of radicals to form the cross-linked polymer.

In an attempt to control the rate of polymerization, *n*-alkyl substituted BPy were used. When short alkyl substituted BPy, such as DMeD or DPrD, was used, the gelation persisted. When the polymerization was carried out using long alkyl substituted Bpy like DPeD or DNoD, soluble polymers could be obtained. Because DNoD provided a higher solubility for Cu(II) species than DPeD did, the rate of polymerization with DNoD

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10.1021/ma011467c CCC: $22.00

Table 1. Emulsion Polymerization of BPEA and CPEA in Various Reaction Conditions

expt	monomer	ligand	temp (°C)	time (h)	conv	M_n	M_w
1	BPEA	Bpy	50	2.5		I[a]	I
2	BPEA	DMeD	50	1.5		I	I
3	BPEA	DPrD	50	3.5		I	I
4	BPEA	DPeD	70	25.0	0.85	11800	68400
5	BPEA	DPeD	100	20.5	0.92	10600	97800
6	BPEA	DNoD	70	11.0	0.61	3580	28600
7	BPEA	DNoD	100	13.0	0.88	10100	62800
8	CPEA	Bpy	70	1.0		I	I
9	CPEA	DMeD	70	1.5		I	I
10	CPEA	DPrD	70	21.0		I	I
11	CPEA	DPeD	70	44.5		N[b]	N
12	CPEA	DPeD	90	44.0	0.81	22100	209500
13	CPEA	DPeD	100	20.5	0.92	19700	95900
14	CPEA	DNoD	70	14.0		N	N
15	CPEA	DNoD	100	9.0	0.76	6570	40100
16[c]	BPEA	DPeD	70	4.0	0.77	4670	6570
17[c]	CPEA	DPeD	90	2.0	0.90	5520	10400

[a] Insoluble. [b] No polymer obtained. [c] Bulk polymerization.

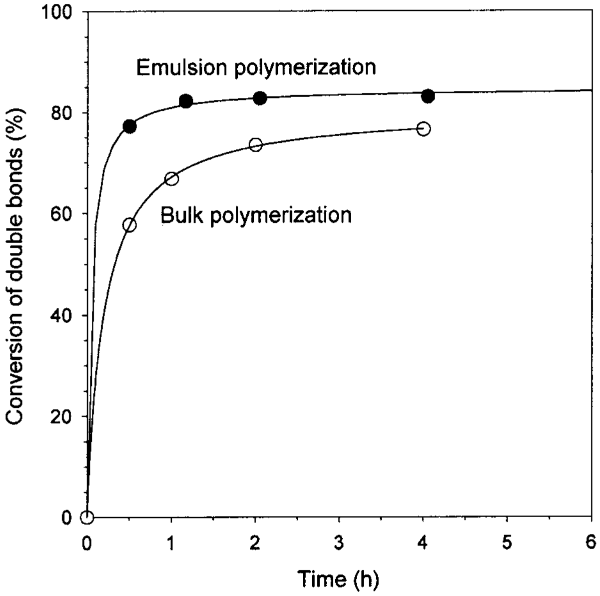

Figure 1. Rate of the polymerizations of BPEA catalyzed by CuBr/DPeD at 70 °C.

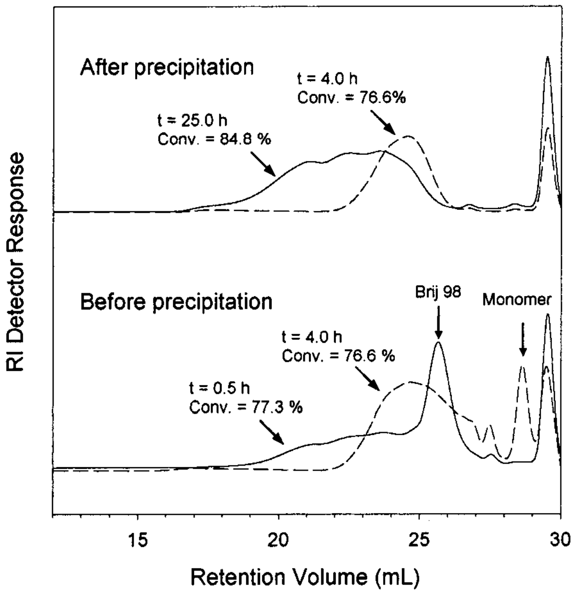

Figure 2. GPC traces for the polymers prepared by emulsion (solid curves) and bulk (dashed curves) polymerization catalyzed by CuBr/DPeD at 70 °C.

was lower, and a high M_n value was obtained only at high reaction temperatures.

The polymerization of BPEA proceeded at a much faster rate than that of CPEA did, which is in agreement with the observation that the R–Br/CuBr initiation system produced a faster rate of polymerization than the R–Cl/CuCl system.[13,14] For example, the polymerization of CPEA with DPeD or DNoD yielded no polymers at 70 °C and was feasible only at higher temperatures.

Figure 1 shows the rates of an emulsion (experiment 4, Table 1) and a bulk (experiment 16) polymerization. The rate of emulsion polymerization was faster than that of bulk polymerization. This result was rather different from that found in the preparation of linear polymers by ATRP, in which the rates of the two polymerizations were found to be nearly identical.[5] In the preparation of the hyperbranched polymer, it can be inferred that the probability of radical termination is lower in emulsion polymerization due to the difference in the mechanism, as will be discussed later. After a rapid initial reaction, both polymerization reactions proceeded at a much slower rate; this is possibly due to the lower accessibility of reactive sites inside the large globular hyperbranched molecule.

In the preparation of hyperbranched polymers using ATRP, the molecular weight of the polymer increased exponentially with time in the same manner as a step growth polymerization, and the sudden onset of cross-linking was observed if a longer reaction time was used.[1] The formation of an insoluble cross-linked polymer may result from the multiple couplings of radicals in different growth chains. This was thought as the reason why only cross-linked polymers or polymers with low molecular weights (M_n < 10 000) were obtained in earlier studies by our group and by others, regardless of whether the polymerization proceeded in bulk or in solution.[1,2,15,16]

Figure 2 shows the GPC traces for the products obtained from an emulsion (experiment 4) and a bulk (experiment 16) polymerization of BPEA. By the emulsion polymerization, a polymer with a higher molecular weight and a broader molecular weight distribution was obtained (after precipitation). While the appearance of broad distribution accompanied to high molecular weight is typical of a hyperbranched polymer,[17,18] the increase in molecular weight by the emulsion polymerization is significant.

Two possible explanations are suggested for why the emulsion polymerization produced higher molecular weight polymers. The first explanation relates to the viscosity of system. The viscosity of the medium in bulk polymerization was so high after 4 h that the reaction could not proceed, whereas it was easy to keep stirring the emulsion polymerization reaction mixture, even after 25 h. The second explanation relates to the mechanism of emulsion polymerization. The polymerization process for preparing a hyperbranched polymer by ATRP proceeds by the repeated stepwise reactions between the radical center and the vinyl group of monomer, dimer, trimer, etc. It is therefore a hybrid of polycondensation and vinyl polymerization.[19] The emulsion polymerization for the hyperbranched polymer in this study may have more of a vinyl polymerization character than a polycondensation character, on consideration that in conventional emulsion polymerization the monomer for the propagation reaction is supplied from monomer droplets via diffusion through the water phase. Therefore, the probability of multiple couplings of radicals in different growing chains is lower in emulsion polymerization than in bulk polymerization. Comparing the polymers sampled at a similar conversion (before precipitation, Figure 2) indicated that the emulsion polymerization proceeded in a different way from bulk polymerization and resulted in a polymer with a much higher molecular weight early in the process.

In summary, emulsion polymerization produced the polymers with higher molecular weight at faster rates in the atom transfer radical polymerization of BPEA and CPEA. The long alkyl substituted bipyridine, DPeD or DNoD, provided good control of the polymerization reaction. Further study for the details of emulsion polymerization of hyperbranched polymers is in progress in this lab.

Acknowledgment. This work was supported by Korea Science and Engineering Foundation through Hyperstructured Organic Materials Research Center and Grant 97-0502-0901-5. S.H.Y. and J.H.L. thank the support by the Brain Korea 21 Program.

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MA011467C