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Synthesis and characterization of ABA triblock copolymers of 2-hydroxyethyl methacrylate and *n*-butyl methacrylate by group transfer polymerization

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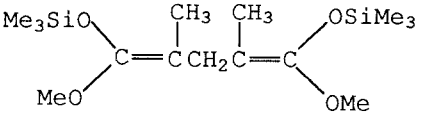
SUMMARY

Difference ABA triblock copolymers(1) of 2-trimethylsilyl-oxyethyl methacrylate(TMS-HEMA) and n-butyl methacrylate(BMA) were prepared by group transfer polymerization(GTP) with a difunctional initiator. The polydispersities of the block copolymers were in 1.16 to 1.43 range. From selective and quantitative hydrolysis of poly(TMS-HEMA) segments of 1, block copolymers(2) of 2-hydroxyethyl methacrylate(HEMA) and BMA could be prepared. 2 showed different solubilities depanding on their compositions. From transmission electron micrographs of films casted from dilute solution of the polymers, it was found that microphase separation of the hydrophilic and hydrophobic domains occurs in different geometries.

INTRODUCTION

Poly(HEMA) is a biomedically important material, and there are many studies for the synthesis of the polymer (1). Among the poly(HEMA)-based polymeric materials, block copolymers of HEMA and a hydrophobic monomer, e.g, styrene have been known as interesting amphiphilic heterophase materials in which hydrophilic and hydrophobic domains are separated (2,3). It has been reported that living polymerization of TMS-HEMA with anionic initiators at low temperature, allows to obtain well-defined poly(HEMA) and amphiphilic block copolymers of the trimethylsilyloxy group (3). Living poly(TMS-HEMA) has been also synthesized by GTP which is a living polymerization of methacrylic monomers at room temperature (4-7). In our earlier report for the synthesis of ABA triblock copolymers consisting of (meth)acylic monomers by GTP, a TMS-HEMA-containing block copolymer has been also reported (8). The present study deals with the synthesis of 1 by GTP with the difunctional initiator, 3. Preparation and characterization of the amphiphilic ABA triblock copolymers,2, is also described.



RESULTS AND DISCUSSION

Copolymer samples 1 were prepared by sequential GTP of the monomers with the difunctional initiator at room temperature. the results of the block copolymerization are summarized in Table 1. Almost quantitative conversions were achieved in all cases. The block copolymers of compartively high molecular weights (above 40,000) could be obtained in 1.16 to 1.43 range, and increased with increasing molecular weight of the polymer. The observed molecular weights of the polymers were somewhat higher than those of theory, which was probably due to the fact that values were calculated with poly(MMA) standards.

Table 1
Synthesis of 1 by GTP with 3[a]

Sample no.[b]	TMS-HEMA composition[c]	$\bar{M}n \times 10^{-3}$ theor.[d,f]	$\bar{M}n \times 10^{-3}$ obsd.[d,e]	$\bar{M}w/\bar{M}n$[d,e]	hydrolyzed product no.
1a	89	7.2	9.2	1.16	2a
1b	79	7.8	10.8	1.19	2b
1c	51	10.2	15.8	1.22	2c
1d	20	9.2	13.7	1.18	2d
1e	61	57.0(17.8)	65.1(21.3)	1.37(1.23)	2e
1f	50	43.6(18.0)	51.2(20.4)	1.39(1.25)	2f
1g	27	53.0(34.7)	63.1(42.9)	1.40(1.35)	2g
1h	79	7.8(6.6)	13.2(8.3)	1.21(1.16)	2h
1i	19	6.0	9.9	1.22	2i
1j	28	40.1(16.0)	51.1(19.2)	1.43(1.25)	2j

a) Initiator; 0.05 mmol of 3, catalyst; $TASHF_2$ (0.1 M in acetonitrile), solvent; THF.

b) 1a-1g; A-B-A triblock copolymers, 1h-1j; B-A-B triblock copolymers where A=poly(TMS-HEMA) and B=poly(BMA).

c) Mol % calculated from monomer feed ratio.

d) The values in parenthesis indicate the $\bar{M}n$'s or polydispersities of the starting polymers; 1a-1g; poly(BMA), 1h-1j; poly(TMS-HEMA).

e) Obtained by GPC using poly(methyl methacrylate) standards

f) $\bar{M}n$ values of theor. were calculated with the ratios of the monomers to the initiator.

As shown in Figure 1, the GPC curvers show that the peak of starting poly(BMA) shifts toward the higher molecular weight side after addition of TMS-HEMA. And the resulting block copolymer still possesses a single peak without shoulder at the lower molecular weight side. The compositions in all block copolymer samples were determined by H-NMR and were found to be

about the same as those calculated from the amount of both monomer feed at the polymerization. There is a possibility of producing a trace of homopolymer of BMA or TMS-HEMA via termination reaction with, e.g. moisture. To separate the homopolymer of BMA with the block copolymer, copolymer sample 2f was stirred overnight in toluene which is a nonsolvent of the block copolymer and a sovent of poly(BMA). However only little decrease (ca. <2%) in weight of the sample was observed. To separate the homopolymer of HEMA with the block copolymer, sample 2j was stirred in THF which is a nonsovent of poly(HEMA). However, there was no precipitate and the solution was clear. From the above results we could conclude that only little homopolymer was produced, in above both cases.

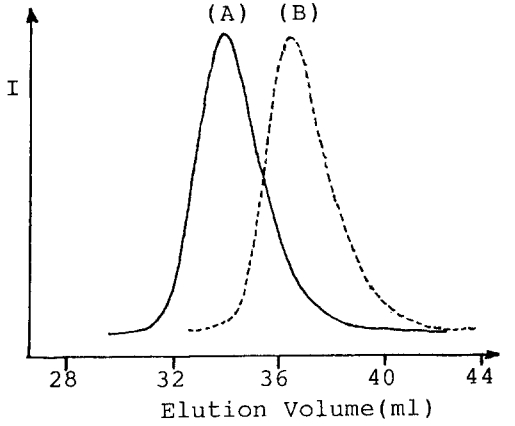


Figure 1. GPC charts of (A) starting poly(BMA) and (B) block copolymer(sample no. 1f) ; flow rate = 1.0 ml of THF/min.

Table 2
Solubilities of 2, and poly(BMA) and poly(HEMA)[a]

solvent	poly(BMA)	block copolymers[b] 2e(28)	2f(50)	2g(61)	poly(HEMA)
toluene	+	-	-	-	-
water	-	-	-	-	-
CCl_4	+	-	-	-	-
CH_2Cl_2	+	+-	-	-	-
THF	+	+	+	+	-
chloroform	+	+-	-	-	-
ethanol	+	+	+	+	+
ethyl ether	+	-	-	-	-
DMF	+	+	+	+	+
acetone	+	+	+	+	-
ethyl acetate	+	-	-	-	-
1,4-dioxane	+	+	+	+	-

a) The symbols (+), (-), and (+-) indicate soluble, insoluble, and swelling, respectively
b) The values in parentheses indicate the mol % of HEMA fraction in the block copolymer.

The deprotection of hydroxyl group was achieved with 0.1N

HCl/methanol at 60°C in methanol solution of the polymer for 1 hr. From the ^{1}H-NMR spectra quantitative desilylation without interfering with the methacrylate ester linkage by the above treatment was confirmed.

Solubilities of 2 are summarized in Table 2. The block copolymers were soluble in THF, DMF, acetone, 1,4-dioxane, and ethanol, and insoluble in toluene, ethyl acetate, diethyl ether, carbon tetrachloride, and water. The block copolymers with low HEMA content were swelling in dichloromethane and chloroform.

Figure 2. Transmission electron micrograph of the film of sample 2f(x72,000).

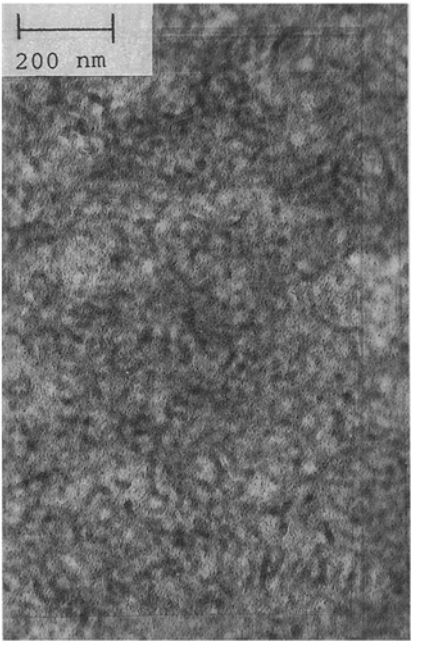


Figure 3. Transmission electron micrograph of the film of sample 2g(x72,000).

Transparent films of 2 could be cast from dilute solutions(5%) in THF-ethanol(1:1(v/v)) mixed solvents. The microstructures of the films could be observed by electron microscopy using osmium tetroxide fixation. The hydrophilic domains, which are composed of HEMA units, were observed as black domains and the hydrophobic domains, composed of BMA units, as white domains in the electron micrographs because HEMA units were fixed selectively by osmium tetroxide as shown in Figure 2 and Figure 3. The lamellar structures of microdomains were observed on the surface of the film of the hydrolyzed sample 2f(Table1), $(HEMA)_{63}$-$(BMA)_{126}$-$(HEMA)_{63}$. The periodicity distance of the lamellar is estimated to be about 25nm, which is a reasonable value for the molecular weight of the copolymer, 3.4×10^4. In the case of hydrolyzed sample 2g(Table1), the

poly(HEMA) domain becomes discontinuous, suggesting lamellar and/or cylinder type microphase separation. The block length of poly(HEMA) and poly(BMA) reflects these morphologycal variation. Incompatibility of the segments in the block copolymer is thus apparent from these results.

EXPERIMENTAL

Materials

Tetrahydrofuran(THF) was distilled from sodium and benzophenone immediately prior to use. TMS-HEMA was prepared by the literature procedure (3). BMA and TMS-HEMA were purified by stirring over finely ground calcium hydride for 2-3 days followed by distillation under reduced pressure. Tris(dimethylamino)sulfonium bifluoride($TASHF_2$) and the initiator 3[1,5-bis(trimethylsilyloxy)-1,5-dimethoxy-2,4 - dimethyl -1,4-pentadiene] was prepared from the literature procedure (4,8)

Polymerization Procedure

For example, a 250 ml three neck flask fitted with an argon inlet, a magnetic stirrer, and a thermocouple was charged with THF(70 ml, via cannular), $THSHF_2$(0.1M in acetonitrile, 0.05 ml), and a difunctional initiator 3(0.2 ml). Then BMA (11.2 ml) was added dropwise via syringe. The temperature rose from 3°C to 17°C. After 10 min additional $TASHF_2$(0.05 ml) was added. After stirring for 1 hr, a 5 ml aliquot of the reaction mixture was withdrawn for analysis. From the aliquot, by evaporation of THF, homopoly(BMA) was obtained ; $\bar{M}n$ = 20,420, $\bar{M}w/\bar{M}n$ = 1,25. To the reaction mixture , TMS-HEMA(16 ml) was added. The temperature rose from 3°C to 8°C. After stirring for additional 5 hrs 5 ml of methanol was added. Then the volatiles were evaported and the resulted polymer was collected ; $\bar{M}n$ = 51,210, $\bar{M}w/\bar{M}n$ = 1.39. The yield of the polymer was quantitative.

Conversion of TMS-HEMA segments into HEMA segments

The block copolymer(5 g) was dissolved in 0.1 N HCl/Methanol(50 ml), and the solution was heated to 60°C for 1hr. After precipitation into water(1,000ml) the polymer was collected and dried at 60°C vacuum over for 24hrs.

Measurements

^{1}H-NMR spectra were reported on a Varian FT 80-A. Molecular weights and polydispersities of 1 were determined by GPC using a Waters 150C with refrative index detector with ultrastyragel columns with THF eluent. The morphology of 2 was investigated by transmission electron microscopy with a JEM 100 CX JEOL.

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