Polymer Bulletin 17, 403–408 (1987)

Polymer Bulletin

Preparation of α,ω-bis(*p*-vinylbenzyl)-terminated polystyrene and α-methylstyrene tetramer

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SUMMARY

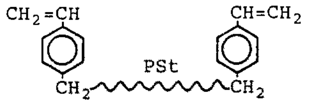
Telechelic macromers composed of only hydrocarbon were prepared by the end-capping reactions of two-ended living polystyrenes and dianion of α-methylstyrene tetramer with *p*-vinylbenzyl chloride. α,ω-bis(*p*-vinylbenzyl)-polystyrene obtained was found to have a narrow molecular weight distribution and high functionality. In the end-capping reaction of the tetrameric dianion, the yield of α,ω-(*p*-vinylbenzyl)α-methylstyrene tetramer was 84 % at most, profoundly depending on the concentration of the dianion. To isolate the functionalized tetramer, the fractional dissolution of a crude product was performed with H_2O/MeOH and the result was desirable.

INTRODUCTION

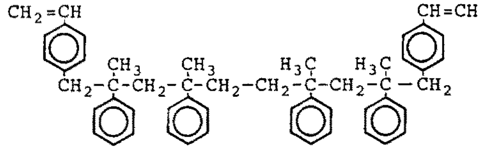
A variety of methods for the synthesis of cross-linked polymer have been developed so far. In cross-linking polymerization involving addition polymerization, one of divinyl or diallyl compounds such as divinylbenzene, ethylene dimethacrylate and diallyl phthalate, has usually been used as a cross-linking agent. These cross-linking agents are of low molecular weight, whereas polymeric cross-linking agents, also known as telechelic macromer, have become of interest in recent years. As to merits of polymeric cross-linking agents, it may be noted that the size of networks can be controlled to a considerable extent by the chain length of telechelic macromer. Moreover, if a different kind of monomer from the polymer chain of the telechelic macromer is used for the cross-linking polymerization, a new type of cross-linked block copolymer should be obtained. The preparation of the cross-linked block copolymer seems to be easily realized only by using a telechelic macromer as a cross-linking agent. Accordingly, this telechelic macromer technique would provide a route to the molecular design of networks, and the more various telechelic macromers are available, the more suitable cross-linked polymer to a requirement can be synthesized.

With respect to telechelic macromers, to our knowledge, several papers have been presented on α,ω-bis(*p*-vinylphenyldimethylsilyl)polystyene (1), α,ω-bis(acrylamido)polyamidoamine (2), α,ω-di(isopropenyl)polyisobutylene (3), α,ω-bis(methacryloyl)poly(1-tert-butylaziridine) (4), α,ω-di(styrene)aromatic polyether sulfone (5). We also have reported on α,ω-bis(*p*-vinylbenzyl)poly(2-vinylpyridine) (6) which is easily and reversibly quaternized to form quaternized water-soluble poly(2-vinylpyridine), i.e., a hydrophilic macromer.

This paper described the preparation of α,ω-bis(*p*-vinylbenzyl)polystyrene (α,ω-BVB-PSt) and α,ω-bis(*p*-vinylbenzyl)α-methylstyene tetramer (α,ω-BVB-(α-MSt)$_4$) which are hydrophobic macromer composed of only hydrocarbon:



α,ω-BVB-PSt



α,ω-BVB-(α-MSt)$_4$

In the preparations of these macromers, we employed a direct end-capping method as in the preparation of (*p*-vinylbenzyl)polystyene macromer (7), paying attention to the narrow molecular weight distribution, high functionality, and wide range of molecular weight of the macromer.

EXPERIMENTAL

Materials and End-Capping Reaction

The Li-, Na-, and K-naphthalene complexes were obtained by the usual method (8). The preparation of α-methylstyrene tetrameric dianion was carried out in the same manner as described by Szwarc et al. (9, 10), in which particular attention was paid on the reaction time (2 h was employed here) and the filtration of the dianion solution. If the reaction time is prolonged and particles of sodium metal remain in the dianion solution, the amount of by-products, i.e., α-methylstyene dimeric and trimeric dianions, increases as pointed out in literature (11). *p*-Vinylbenzyl chloride (*p*-VBC) was synthesized according to one (12) of the known methods and purified as previously reported (6). THF used as solvent was purified by distillation in vacuo in the presence of the sodium salt of the benzophenone dianion.

The preparation and end-capping reaction of two-ended living polystyrene were carried out in a high-vacuum system (10^{-5} torr) by using the same apparatus as described previously (13). In these procedures, effective mixing of the reactant solutions is important for a narrow molecular weight distribution and a high functionality of α,ω-BVB-PSt macromer.

Measurement and Characterization

Gel permeation chromatograph (GPC) was performed at a column-oven temperature of 38°C on a Toyo Soda HLC-802UR with two GMH$_6$ columns or G2000H$_8$ and G3000H$_8$ columns (Toyo Soda, Japan). THF was used as the eluent, and the flow rate was 1.0 mL/min. The molecular weight distributions (M_w/M_n) of the polymers were calculated from their GPC curves by using a calibration curve constructed from polystyrene standards. The functionalities of the macromers were determined as described previously (7). The yields of α,ω-BVB-(α-MSt)$_4$ and the dimeric-terminated product of α-methylstyene tetrameric dianion were evaluated from their GPC peak areas (RI detector).

RESULTS AND DISCUSSION

Preparation of α,ω-BVB-PSt

Two-ended living polystyrenes having Li^+, Na^+, and K^+ as counterions were prepared by the polymerizations of styrene in THF by using Li-, Na-, and K-naphthalene complexes as initiator, respectively. These processes were carried out at 0°C to arrest the termination of living polystyrenes (especially, polystyryllithium) with THF (14). The resulting living polystyrenes were allowed to react with *p*-VBC for the introduction of *p*-vinylbenzyl groups at their both ends, i.e., for the preparation of telechelic polystyrene macromer. The conditions of the polymerization and this end-capping reaction are listed in Table 1. The reason why a large excess of *p*-VBC was used is that in preliminary experiments the GPC curves of products obtained at [*p*-VBC]/[LE] < 2.5 were very broad indicating the formation of polymer having a molecular weight higher than expected one. Table 2 shows the results of the characterization of the macromers obtained. The molecular weights of the macromers determined by VPO and GPC are in agreement with those calculated on the basis of [M]/[I], the conversion, and the molecular weight of α- and ω-vinylbenzyl groups. Naturally, the molecular weight of α,ω-BVB-PSt can be controlled by [M]/[I]. The functionality of α,ω-BVB-PSt prepared by using living polystyene with any counterion of Li^+, Na^+, and K^+ is regarded as 2, allowing for experimental error. Figure 1 demonstrates a change of GPC curves before and after the end-capping reaction of polystyryllithium (Expt PS-1) as an typical example. There is no broadening of the GPC curve (Fig. 1-a as compared with 1-b) by chain extention due to addition of polystyryllithium to the vinyl group of *p*-VBC, and Curves a' and b' in Figure 1 indicate that the recovered polymer after the reaction with *p*-VBC is much higher sensitive to a UV detector of GPC than the original. These results also support that the S_N2 reaction of the living ends with the chloromethyl groups of *p*-VBC takes place predominantly.

Table 1

Preparation of α,ω-BVB-PSt Macromer by End-Capping Reaction of Two-Ended Living Polystyrene with *p*-VBC in THF

	Living PSt soln[a]					*p*-VBC soln		
Expt	initiator	(mmol)	St (mmol)	[M]/[I]	[LE][b] (mmol/L)	[*p*-VBC] (mol/L)	[*p*-VBC]/[LE][b]	Polymer yield (%)
PS-1	Li-Naph	0.283	11.8	41.7	14.9	0.864	6.68	99
-2	"	2.23	126	56.5	27.3	0.864	11.2	100
-3	"	0.425	32.5	76.5	18.3	0.852	5.96	97
-4	Na-Naph	1.10	20.0	18.2	68.2	0.864	8.52	93
-5	"	1.08	43.0	39.8	35.7	0.864	4.47	96
-6	"	0.201	58.0	289	5.02	0.852	8.29	99
-7	K-Naph	0.332	13.8	41.6	15.0	0.864	6.23	98

[a] Polymerization time., 0°C; time, 20-60 min.
[b] Concentration of living ends.

Table 2

Characterization of α,ω-BVB-PSt Macromer

	$M_n \times 10^{-3}$				
Expt	calcd	VPO	GPC	M_w/M_n[a]	f[b]
PS-1	8.83	9.5	10	1.2_0	2.0_4
-2	12.0	13	13	1.1_6	1.8_1
-3	15.7	—	16	1.1_7	1.9_5
-4	3.76	4.0	4.2	1.2_3	2.0_0
-5	8.19	9.4	9.0	1.1_7	2.0_1
-6	59.8	—	61	1.1_6	1.8_9
-7	8.73	9.2	8.5	1.1_8	2.0_7

[a] From GPC data.
[b] Functionality (C=C/molecule).

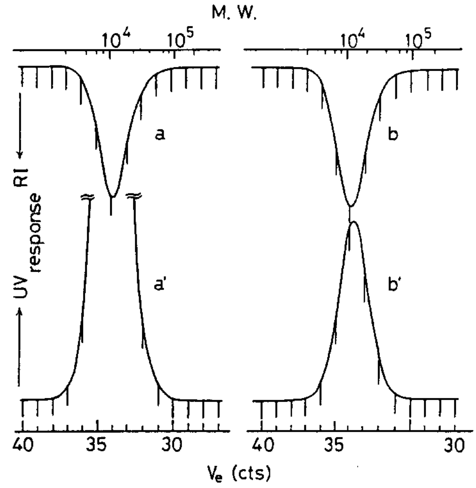


Figure 1. GPC curves of polymers before (b) and after (a) the end-capping reaction in Expt PS-1.

Preparation of α,ω-BVB-(α-MSt)$_4$

For the synthesis of telechelic polystyene macromer with both low molecular weight and narrow molecular weight distribution by the above method, it is necessary to prepare two-ended living oligostyrene which has a narrow molecular weight distribution. However, the preparation of such oligostyrene is very difficult owing to the high rate of propagation of styrene. Thus, we employed dianions of α-methylstyrene tetramer as homologue of living oligostyrene for preparation of hydrophobic telechelic macromer with a low molecular weight.

The end-capping reaction of the tetrameric dianion was carried out with *p*-VBC. The results are summarized in Table 3 along with reaction conditions. Figure 2 demonstrates the dependence of yields of α,ω-BVB-(α-MSt)$_4$ on the concentrations of living ends. Figure 3 shows the GPC curves of protonated original tetrameric dianion and of the recovered oligomers after the end-capping reactions (Expts MS-4 and -5). These results reveal that the yield of α,ω-BVB-(α-MSt)$_4$ is largly dependent on the concentration of living ends whereas independent of that of *p*-VBC in the range of its concentrations used. That is, when the concentration of the living ends was higher than 0.05 mol/L, a large portion of the product had molecular weights larger than expected one (Fig. 3-b), suggesting that the addition reaction of living ends to vinyl groups occurred to a considerable extent. To the contrary, when the concentration of living ends was low, e.g., in the case of Expt MS-5, the GPC curve of the products was primarily composed of two peaks (Fig. 3-c) and the main peak was very sharp and its elution counts corresponded to that of molecular weight of α,ω-BVB-(α-MSt)$_4$. The other peak was in agreement with that of molecular weight of (VB)$_3$-(α-MSt)$_8$, which would be formed by the addition reaction of living end with the vinyl group of *p*-VBC followed by the S_N2 reaction of living end with its chloromethyl group.

The solution of the dianions of α-methylstyrene tetramer used in this work also contained a small amount of dianion of α-methylstyrene trimer as pointed out in literature (11) and as shown in Figure 3-a. However, no peak due to α,ω-BVB-(α-MSt)$_3$ appeared in the GPC curves of the recovered oligomers from a precipitant of MeOH/H_2O (3/1 v/v). It may remain in the precipitant.

Table 3

Preparation of α,ω-BVB-(α-MSt)$_4^{a)}$

				α,ω-BVB-(α-MSt)$_4$	
Expt	(α-MSt)$_4^{--}$ soln [LE] (mmol/L)	*p*-VBC soln [*p*-VBC] (mol/L)	[*p*-VBC] / [LE]	yield (%)	f
MS-1	16	2.11	14.7	82	—
-2	48	2.11	15.0	84	—
-3	94	2.11	13.2	70	—
-4	263	0.690	3.22	27	—
-5	46	1.97	7.80	83	2.0_5
-6	46	1.01	7.84	82	2.0_5
-7	46	0.494	7.76	82	2.1_3
-8	46	0.210	7.96	80	2.1_2

[a] Reaction temp., 0°C; time, 0.5 h; solvent, THF.

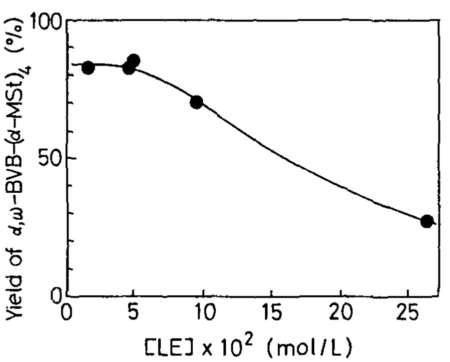


Figure 2. Relationship between the yield of α,ω-BVB-(α-MSt) and the concentration of living ends.

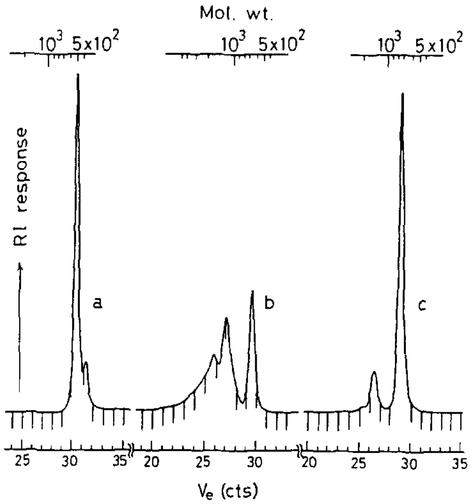


Figure 3. GPC curves of protonated α-methylstyrene tetrameric dianion (a), recovered oligomers in Expt MS-4 (b), and -5 (c).

Since the dimeric termination of tetrameric dianions was found to be unavoidable as shown in Figure 2, the fractionation procedure of the products is necessary for obtaining pure α,ω-BVB-(α-MSt)$_4$. For this reason, a fractional dissolution was tried; i.e., 200 mg of the ground crude product of Expt MS-6 and 260 mL of H_2O/MeOH (H_2O, 8 vol%) mixture were placed in a 300-mL Erlenmeyer flask and stirred for 24 h at ambient temperature. The insoluble part was filtered and the mother liquor was evaporated till the soluble part precipitated. The precipitate was filtered and dried in vacuo for 24 h. The yield was 113 mg. The GPC traces of insoluble and soluble parts thus obtained are shown in Figure 4. These curves indicate that α,ω-BVB-(α-MSt)$_4$ can be isolated from the crude product by this simple fractional dissolution, although the insoluble part contains α,ω-BVB-(α-MSt)$_4$ to a considerable extent (Fig. 4-b).

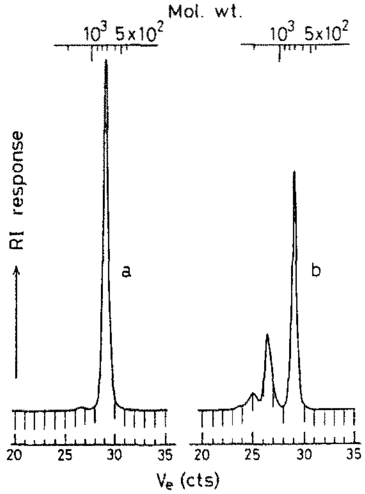


Figure 4. GPC traces of soluble (a) and insoluble (b) parts in the fractional dissolution of a crude product in the end-capping reaction (Expt MS-6).

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Accepted April 1, 1987 S