In other solvents there are variable positive contributions to the measured radius of gyration from the rest of the molecule. If it is assumed that the segment distribution is normal and is at least approximately gaussian, then in solvents such as MIBK or THF, of refractive index far from either polymer component, for polymer SI-a-6, R_{ap}^2 will be close to the true value.

$$R_{ap}^2(\text{MIBK}) = 1.07R_a^2 + 0.92R_b^2 \qquad (11)$$

The actual radius of gyration on these assumptions is simply $R_a^2 + R_b^2$, with $\overline{G_aG_b}^2 = 2(R_a^2 + R_b^2)$.[33] If it is assumed that, as in chlorobenzene, R_a^2 and R_b^2 are unchanged from their values in the corresponding homopolymers, these can be calculated from data on polymer M-11 and estimated for isoprene from viscosity data.[34] The value calculated ($R_{ap}^2 = 10.5 \times 10^4$ Å^2) is appreciably lower than that observed (14.7×10^4 Å^2) in MIBK. This difference becomes smaller in good solvents such as benzene. Unfortunately, it is not possible to decide if the discrepancy in MIBK is caused by individual coil expansions caused by the presence of the other component in this poor solvent or by the formation of a more separated structure. In any case, it is clear that even gaussian statistics naturally provide some separation of the two polymer components. The mean-square distance between their centers of mass is twice the total radius of gyration. The results in chlorobenzene obviously require some separation of the two types of monomer unit, but whether this is produced by normal sequence distributions or is in a more exaggerated form cannot be decided by the present data.

[33] M. Leng and H. Benoit, *J. Chim. Phys. Physicochim. Biol.*, **58**, 480 (1961).

[34] J. Prud'homme, J. E. L. Roovers, and S. Bywater, unpublished data.

Block Copolymerization. III. Syntheses of Multiblock Copolymers of Polytetrahydrofuran and Polystyrene by Ion Coupling

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ABSTRACT: Multiblock copolymers of an $(AB)_n$ type were prepared by ion coupling of the polytetrahydrofuran (THF) dication and the polystyrene (St) dianion. The poly-THF dication was prepared by the polymerization of THF with 2,2′-octamethylene bis-1,3-dioxolenium perchlorate as a bifunctional initiator. The poly-St dianion was prepared by carboxylating the living polymer of St in THF initiated with α-methylstyrene tetramer dianion. The formation of multiblock elastomers such as $(\text{THF}_{110}\text{–St}_{53})_{30}$ by ion coupling is a good indication of the high purity of the poly-THF dication and the poly-St carboxylate dianion.

Since the discovery of the cationic living polymer of tetrahydrofuran (THF), a unique method for forming a block copolymer by linking cationic living polymer with anionic living polymer has been suggested.[1] The present investigation aims at the synthesis of a multiblock copolymer of an $(AB)_n$ type by ion coupling of the poly-THF dication and the polystyrene (poly-St) dianion. Such an approach can prove the formation of the living polymer of THF, and is also useful for the syntheses of novel block copolymers. Although some multiblock copolymers have been prepared by condensation, a block copolymer consisting of long and well-characterized sequences is expected to present some information about structure–property relationships.

Although previous work suggested the possibility of ion coupling, it was still insufficient to prove the absence of homopolymers. Berger, Levy, and Vofsi[1] and, independently, Asami and Chikazawa[2] treated poly-THF cations with poly-St anions, and the partial formation of THF–St or THF–St–THF block copolymers was characterized by fractional precipitation. Although the poly-St dianion can be prepared easily by using the α-methylstyrene tetarmer dianion, a new bifunctional initiator is necessary to prepare the poly-THF dication. In previous papers,[3] we reported the formation of poly-THF dication by using bisdioxolenium perchlorate initiator. To obtain a multiblock copolymer, ion coupling must proceed without any side reactions, and some modification of the poly-St dianion was studied. The preparation of the initiator, the polymerization, and the ion coupling reaction were carried out in a high-vacuum system (10^{-6} mm).

Experimental Section

Materials. α-Methylstyrene (MS) and styrene (St) were purified in the usual manner, dried with calcium hydride in a high-vacuum system, and distilled into a small ampoule. Tetrahydrofuran (THF) was refluxed over sodium metal and sealed in an ampoule after distillation from a green-colored solution of sodium naphthalene in a high vacuum system. Ethylene oxide (EO) was dried over calcium hydride and distilled into a small ampoule in a high-vacuum system. Carbon dioxide gas was purified by passing through a silica gel–calcium chloride packed column in a high-vacuum system, and sealed in an ampoule.

Preparation of Cationic Initiator. 2,2′-Octamethylenebis-1,3-dioxolenium perchlorate (OMDO-ClO$_4$) was prepared by the addition of bis-2-bromoethyl sebacate to the dry nitromethane solution of silver perchlorate as described in a previous paper.[3]

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[1] G. Berger, M. Levy, and D. Vofsi, *J. Polym. Sci., Part B*, **4**, 183 (1966).

[2] R. Asami and M. Chikazawa, Papers presented at the 19th Annual Meeting of the Chemical Society of Japan, 1966, No. 4T022.

[3] (a) Y. Yamashita, M. Hirota, K. Nobutoki, Y. Nakamura, A. Hirao, S. Kozawa, K. Chiba, H. Matsui, G. Hattori, and M. Okada, *J. Polym. Sci., Part B*, **8**, 483 (1970); (b) Y. Yamashita, M. Hirota, H. Matsui, A. Hirao, and K. Nobutoki, *Polym. J.*, **2**, 43 (1971).

The concentration of the initiator was determined by weighing the solute after evaporation of the solvent.

Preparation of the Poly-THF Dictation. An aliquot of a nitromethane solution of the bifunctional cationic initiator was placed in a flask as shown in Figure 1. The nitromethane was evaporated and THF was added through a break-seal. The bulk polymerization was carried out at 0°.

Preparation of Polymer Dianion. Living α-methylstyrene tetramer (MS_4)[4] was prepared by the reaction of MS with sodium evaporated onto the glass surface of the flask in THF at −20° *in vacuo*. Then the living polymer solution was filtered through sintered glass and divided into ampoules. The concentration of the living polymer was determined by the acid titration method and by weighing of the residual polymer after evaporation of the solvent. Living polystyrene was prepared by gradual addition of a THF solution of St into living MS_4 solution at 0°. Poly-St dialkoxide anion was prepared by the reaction of living poly-St and ethylene oxide *in vacuo*. MS_4 and poly-St dicarboxylate anions were prepared by introducing carbon dioxide through a break-seal into a THF solution of living polymer, and excess carbon dioxide was removed under reduced pressure.

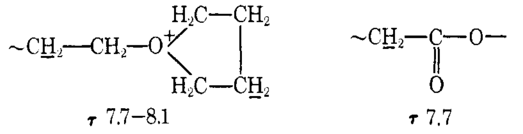
Ion-Coupling Reactions. The ion-coupling reactions of polymer dianions and dications were carried out in a high-vacuum system, as shown in Figure 1. After evacuating the system, a nitromethane solution of the cationic initiator was transferred through a break-seal into a flask. The solvent was evaporated and the system was sealed at a. Then THF was added to the cationic initiator and polymerization was carried out while stirring the mixture at room temperature. An aliquot of the poly-THF solution was transferred into an amopule and sealed at b. Ion coupling was carried out by addition of a THF solution of the poly-St dianion to the poly-THF dication with stirring at room temperature. After several hours, the reaction was terminated by pouring into the mixture a large amount of methanol. The crude polymer was reprecipitated from benzene–methanol and freeze-dried from benzene solution. Poly-THF homopolymer was extracted with hot isopropyl alcohol. The block copolymer is a brown rubbery mass which is soluble in THF, benzene, and chloroform, but insoluble in methanol. In the case of the PTHF–MS_4 system, the reprecipitated polymer was soluble in hot isopropyl alcohol. However, no further separation was carried out.

Characterization. Number-average molecular weights were measured in benzene using a Hitachi vapor pressure osmometer, Model 115, or a Hewlett-Packard 502 high-speed membrane osmometer. Nmr spectra were recorded in carbon tetrachloride at 60° on a Japan Electron Optics spectrometer, Model C-60, operating at 60 Mc. Ir spectra were recorded with polymer films on a Japan Spectroscopic infrared spectrophotometer, Model IR-S. Gel permeation chromatograms were measured in THF using a Waters Model 200.

Results and Discussion

Reaction of the Cationic Living Polymer of THF and the Anionic Living Polymer of St. The poly-THF dication was prepared by bulk polymerization of THF at room temperature in less than 20% conversion by using 2,2′-octamethylenebis-1,3-dioxolenium perchlorate (OMDO-ClO_4) as an initiator. α-Methylstyrene tetramer (MS_4) dianion was prepared from MS and sodium in THF at −20°. Poly-St dianion was prepared by the polymerization of St in THF by MS_4 dianion.

The reaction of equimolar amounts of poly-THF dication and MS_4 dianion in THF was carried out and the molecular weight of the methanol-insoluble fraction was found to be increased a little from that of the parent homopolymer. The ir spectrum of the product showed characteristic absorptions at 1710 cm^{-1}, due to the C=O stretch of the aliphatic ketone, and at 1740 cm^{-1}, assignable to the ester carbonyl of the initiator fragment. The electron densities on the α-carbon atom of the oxonium ion and on the carbonyl carbon atom were compared using the nmr chemical shifts of the protons on neighboring carbon atoms (shown below underlined). The electron density on the α-carbon atom of the oxonium ion might be higher than that on the carbonyl carbon atom, and the MS_4 carbanion might attack the ester group in the polymer chain rather than the oxonium ends of poly-THF, yielding the ketone group after chain fission.



τ 7.7–8.1

τ 7.7

Despite the partial success of ion coupling observed by Berger, *et al.*,[1] and by Asami, *et al.*,[2] the polystyryl anion might abstract an α proton of the oxonium ion to form poly-St and poly-THF mixtures. A recent development in the phenoxyl end-capping method for determination of the concentration of the cationic living end by Saegusa and Matsumoto[5] has proved the quantitative occurrence of ion coupling between sodium phenoxide and the poly-THF cation. The attempted reaction of the poly-THF dication with the less nucleophilic poly-St dialkoxide anion, prepared from the poly-St dianion and ethylene oxide, failed to increase the molecular weight of the parent homopolymer. The alkoxide anion is probably still too nucleophilic and attacks the ester carbonyl group to form another ester bond without chain extension, leading to some poly-St and poly-THF mixtures.

Preferential attack of poly-St dianion on the oxonium ion in the presence of an ester group is expected with the carboxylate anion, because no reaction was observed between the ester and the carboxylate anion. Thus the living carbanion was modified by treating it with carbon dioxide.

Ion Coupling of the Poly-THF Dication and the MS_4 Dicarboxylate Anion. To examine the reaction conditions of ion coupling, the reaction of the poly-THF dication and the MS_4 dicarboxylate anion was carried out in THF at room temperature for 10 hr, varying the molar ratios of the reagents. The results are shown in Table I and Figure 2. Ion coupling was indicated by the precipitation of $NaClO_4$ and also by a gradual increase in the viscosity of the solution. The rate of the ion coupling reaction between the oxonium ion and the carboxylate ion is slow.

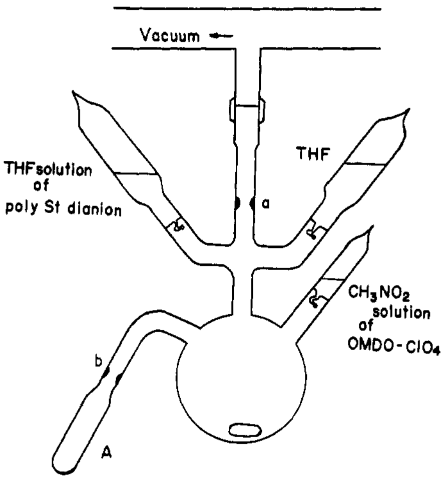


Figure 1. Ion-coupling apparatus.

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[4] C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **66**, 904 (1962).

[5] T. Saegusa and S. Matsumoto, *J. Polym. Sci., Part A-1*, **6**, 1559 (1968).

TABLE I
ION COUPLING OF THE POLYTETRAHYDROFURAN DICATION AND THE α-METHYLSTYRENE TETRAMER DICARBOXYLATE ANION[a]

Run no.	OMDO-ClO$_4$, mol × 10^4	MS$_4$, mol × 10^4	THF, ml	Cationic initiator, mol %	Block copolymer, g	PTHF, g	$\bar{M}_n$ of block copolymer	Repeating unit, n[b]
1	3.12	6.16	12.4	33.6	4.79	0.10	8.4 × 10^4	6.2
2	3.12	4.34	8.8	41.8	5.21	0.22	12.0 × 10^4	8.9
3	3.12	3.08	6.2	50.3	5.50	0.11	53.0 × 10^4	39.4
4	3.12	2.19	4.4	58.8	4.95	0.12	16.0 × 10^4	11.9
5	3.12	1.60	3.2	66.2	6.73	0.23	22.0 × 10^4	16.3

[a] Polymerization of THF: THF 30 ml, 0°, 60 hr, yield of PTHF 4.03 g, $\bar{M}_n$(calcd) of PTHF 12,900, $\bar{M}_n$(calcd) of MS$_4$ dicarboxylate anion 560. Ion coupling, room temperature, 1 hr. [b] Calculated from (THF–MS$_4$)$_n$.

TABLE II
ION COUPLING OF THE POLYTETRAHYDROFURAN DICATION AND THE POLYSTYRENE DICARBOXYLATE ANION

	Run no.					
	1	2	3	4	5	6
Cationic initiator, mol × 10^5	2.23	1.11	3.96	4.48	8.45	95
Anionic initiator, mol × 10^5	2.23	2.22	4.26	4.48	7.98	77
Ion coupling, hr	2	3	18	67	55	15.5
PTHF, g/THF, ml	0.08/16.5	0.29/19.1	0.77/18.1	3.68/64.8	8.17/90.1	5.80/32.6
THF conversion, %	0.51	1.69	5.46	6.39	10.2	20.4
PSt, g/THF, ml	1.63/21.6	1.63/21.4	1.19/13.7	1.19/14.5	3.12/31.9	3.06/27.0
THF homopolymer, g	0.03	0.02	0.04	0.36	0.43	0.70
Block copolymer, g	1.69	1.90	1.94	4.76	10.90	9.91
$\bar{M}_n$ × 10^{-4} THF	0.4	2.6	2.2	8.2	11.1	0.8
St	12.3	12.3	2.7	2.7	6.0	0.5
Block copolymer	13.2	12.0	9.6	19.6	50.2	40.0
(THF–St)$_n$, n	1.1	0.8	2.0	1.8	2.9	30
St content, mol %	94	81	48	12	24	33

The highest molecular weight of the block copolymer was 53.0 × 10^4 at a 1:1 feed ratio. The number of repeating units n in (THF–MS$_4$)$_n$ is 39. Ion coupling is a kind of polycondensation, and the degree of polymerization, P_n, at high conversions is expressed by the following equation, where r denotes the molar feed ratio of the reactants.

$$P_n = (1 + r)/(1 - r) = 2n$$

In the case of an equimolar reaction, $P_n = 1/(1 - p)$, where p denotes the extent of the reaction. The agreement between the observed and calculated P_n values in Figure 2 shows similar high purity of both reagents, and that the extent of the reaction, p, was 98.7% based on the catalyst concentration. In other words, almost every catalyst molecule formed one living polymer molecule. In the case of higher dication feed ratio, the polymerization of THF by the remaining cation occurred during the ion-coupling reaction. This is supported by the observation that the yield and the molecular weight of the block copolymer has increased unexpectedly in run no. 5 of Table I.

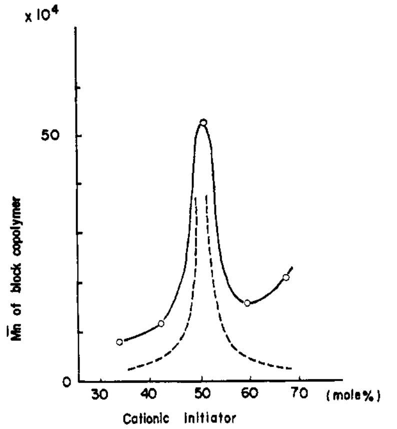
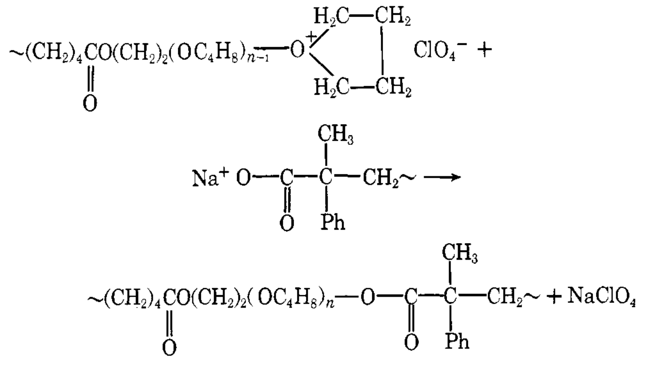


Figure 2. Effect of molar ratio of initiators on the $\bar{M}_n$ of the block copolymer (THF–MS$_4$)$_n$.

The nmr spectrum of the block copolymer is very similar to that of the THF homopolymer. The ir spectrum of the block copolymer showed characteristic absorptions at 1740 cm^{-1} due to the ester carbonyl group of the initiator fragment and the linking bond formed by coupling, at 700 and 1600 cm^{-1} to the phenyl group, and at 1110 cm^{-1} to the C–O–C stretching band of poly-THF. From these facts the following reaction scheme can be postulated for ion coupling.



Ion Coupling of the Poly-THF Dication and the Poly-St Dicarboxylate Anion. The results of ion coupling of the poly-THF dication and the poly-St dicarboxylate anion are shown in Table II. Small amounts of THF homopolymer

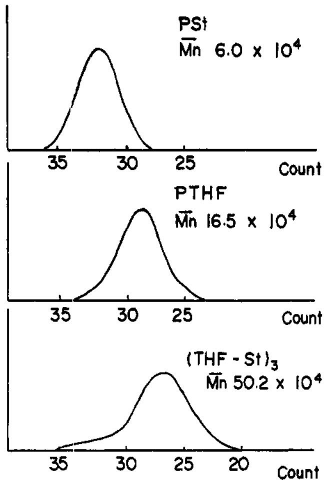


Figure 3. Gel permeation chromatogram of the (THF–St)$_3$ block copolymer and the parent homopolymers.

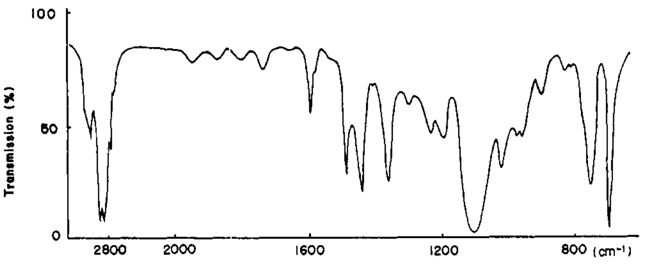


Figure 4. Infrared spectrum of the (THF–St)$_n$ block copolymer (no. 3).

were extracted with boiling isopropyl alcohol, and although separation of some St homopolymer from the block copolymer was not easy, high purity of the block copolymer is proposed in the following discussion.

The number of repeating units n in (THF–St)$_n$ varies from 30 in no. 6 to 2 or 3 in no. 3–5. The failure of ion coupling in no. 1 and 2 may be due to insufficient reaction time. The decrease in the number of repeating units in the THF–St system in the case of high-molecular-weight reagents might be ascribed to the difficulty of ion coupling between high-molecular-weight species. However, this reaction could not be diffusion controlled because the rate constant of the reaction does not exceed 10 l./(mol sec), as indicated by the apparent slow rate. Probably, the low concentration of the reagent (10^{-4} M) leads to a slow coupling rate, and also some termination by impurities might be unavoidable.

Gel permeation chromatograms of poly-St, -THF, and the block copolymer are shown in Figure 3. Poly-THF shows a little broader molecular weight distribution compared with the monodisperse poly-St, owing to the slow rate of initiation.[3]

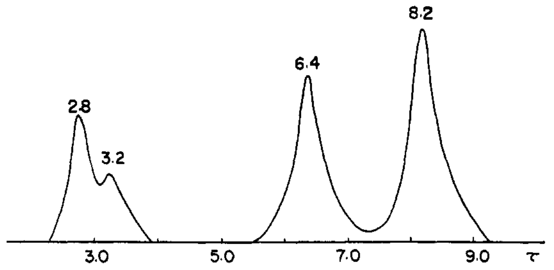
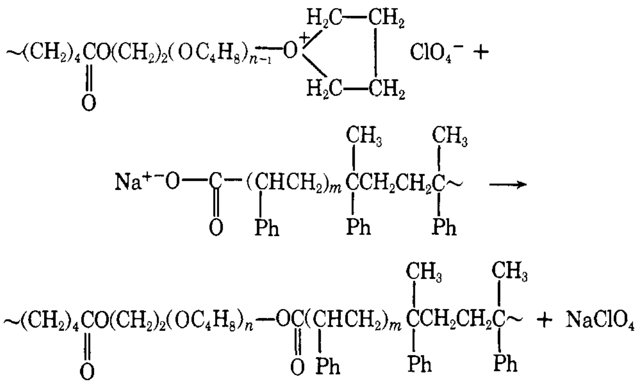


Figure 5. Nmr spectrum of the (THF–St)$_n$ block copolymer (no. 3).

The molecular weight distribution of the block copolymer corresponds to the observed $\bar{M}_n$. However, the distribution seems a little narrower than the most probable distribution expected for this type of the polycondensation.

The ir spectrum of the block copolymer is shown in Figure 4. It shows characteristic absorptions at 1740 cm^{-1}, corresponding to the ester carbonyl group of the initiator fragment and the linking bond formed by coupling, and at 1110 and 700 cm^{-1} due to poly-THF and poly-St, respectively. The nmr spectrum in Figure 5 shows the characteristic signals at τ about 3 for the phenyl protons and 6.4 for the α protons of poly-THF and 8.2 for the methine and methylene protons of poly-St and the β protons of poly-THF. The St content of the block copolymer was calculated from the ratio of the peak areas in the nmr spectrum. The small discrepancies between the calculated and observed values might be attributed to end group effects caused by inaccurate feed ratios or to excess polymerization of THF during the slow ion-coupling reaction.

Thus, the formation of the multiblock copolymer (THF–St)$_n$ is depicted by the following scheme.



Although the position of the catalyst fragment in the poly-THF segment is obscure because of the slow initiation rate,[3] the formation of 60-segment copolymers (THF$_{110}$–St$_{53}$)$_{30}$ is a good demonstration of the usefulness of ion-coupling reactions.