Table VII
Fractionation Results of Recovered Polymer (Ex. SOL-5)

	Weight		No.-average molecular weight $\overline{M}_n \times 10^{-4}$	
	mg	%		
Fraction I (Homopolystyrene)	252	63.0	2.61	(2.41[a])
Fraction II (Graft polymer)	145	36.3	38.3	(82.9[b])

[a] Of terminated living polystyrene used in this grafting reaction, for reference. [b] Of graft polymer which is expected from the extent of coupling of epoxide ring, for reference.

small compared with that of living polystyrene, the ratio of the area of the peak of the graft polymer to total area of the two peaks may indicate the extent of coupling of living polystyrene. The extent of coupling so determined for Exs SOK-2 and SOL-23 is 59.7 and 76.5%, respectively.

The turbidimetric titration curves of the polymers obtained in Exs SOL-1 and SOL-5 have a clear inflection point as shown in Figure 7 so that both parts before and after this point can be distinguished easily. The part before the inflection corresponds to the graft polymer and may also represent the extent of grafting (Ex SOL-1, 53%; Ex SOL-5, 31%) for the same reason given in the discussion of the GPC data. The part after the inflection corresponds to the uncoupled living polystyrene.

Table VII shows the results of the fractional precipitation. In a single fractionation, the number-average molecular weight of fraction I was approximately equal to that of the living polystyrene used. On the other hand, the number-average molecular weight of fraction II was about half of that of the graft polymer ($\overline{M}_n = 82.9 \times 10^4$) estimated from the extent of coupling of epoxide ring (57%). However, the discrepancy may be explained by taking into account 3.5 wt % of uncoupled living polystyrene ($\overline{M}_n = 2.47 \times 10^4$) in the graft polymer. Therefore, the fractionation seems to have been carried out satisfactorily, and the weight percent of fraction II (36.3%) should be approximately equal to the extent of grafting of living polystyrene because, as mentioned above, the amount of backbone polymer used was negligibly small compared with that of living polystyrene.

In the GPC and the turbidimetric titration curves, the graft polymer and the uncoupled living polystyrene were distinguished easily owing to the great difference in their molecular weight which arose from the high degree of coupling. The same reason may be given for the easy separation of the respective polymers in the fractional precipitation and for the good agreement[2] of the extent of grafting calculated from eq 1 with that determined by the above characterizations.

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Coupling Reaction between Living Polystyrene and Poly(chloromethylstyrene)[1]

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ABSTRACT: The coupling reaction between living polystyrene and poly(chloromethylstyrene), P(CMS), was investigated with emphasis on the coupling reactivity of P(CMS) as a multifunctional backbone polymer for the preparation of well-defined polymer. The backbone polymer was prepared by the radical polymerization of commercially available chloromethylstyrene. High extent of coupling (>80%) is attained in tetrahydrofuran/benzene (44/56 vol %) mixture with Li^+ as the counterion and at low values of the mole ratio of living ends to chloromethyl groups, [LE]/[CH_2Cl], in the case of K^+. The extent of side reactions is large at high values of [LE]/[CH_2Cl] or in a P(CMS)–poly(styryllithium)–benzene system. The solvent, the counterion, and the reaction temperature all affect the extent of coupling mainly by changing the ionic character of the living polystyrene.

A chloromethyl group of benzylic type is one of the functional groups that has often been used for the preparation of well-defined polymers such as star and graft polymers by means of nucleophilic substitution with living polymers. For the preparation of star polymers, tri(chloromethyl)benzene,[2] tetra(chloromethyl)benzene,[3,4] hexa[*p*-(chloromethyl)phenyl]benzene,[5] and chloromethylated polystyrene (low degree of polymerization)[3] have been used as the multifunctional centers. For graft polymers, i.e., comb-shaped polymers, only chloromethylated polystyrene[3,6-12] has been used.

Altares et al.[3] treated poly(styryllithium) (PSt-Li) with tetra(chloromethyl)benzene or chloromethylated polystyrene

Table I
Coupling Reaction between Living Polystyrene and P(CMS)

Expt	Living PSt $[LE]$[a] $\times 10^3$, mol L^{-1}	P(CMS) $[CH_2Cl]$[b] $\times 10^3$, mol L^{-1}	$[LE]/[CH_2Cl]$	Reaction Temp, °C	Reaction Time h	$(\overline{M}_n)_R$[c] $\times 10^{-4}$	Extent of coupling, % LE[d]	Extent of coupling, % CH_2Cl[e]
	PSt-K[f]							
K-1	1.92	9.80	0.196	0	71	24.3	91.0	17.8
K-2	2.96	6.65	0.445	0	71	12.9	80.2	35.7
K-3	3.11	6.21	0.501	0	71	11.9	79.5	39.8
K-4	3.34	5.51	0.606	0	71	11.4	78.5	47.6
K-5	3.65	4.58	0.797	0	71	9.58	74.5	59.4
K-6	3.86	3.96	0.975	0	161	8.05	69.4	67.7
K-7	4.07	3.33	1.22	0	238	5.52	57.6	70.3
	PSt-Li[g]							
L-1	1.96	10.4	0.188	23	42	9.68	77.3	14.5
L-2	3.08	7.67	0.402	23	42	9.00	75.2	30.2
L-3	3.41	6.84	0.499	23	118	8.14	72.5	36.1
L-4	3.74	6.03	0.620	23	227	7.85	71.5	44.3
L-5	4.13	5.07	0.819	23	381	7.07	68.3	55.9
L-6	4.39	4.40	0.998	23	381	6.95	67.7	67.6
L-7	4.65	3.77	1.23	23	382	5.35	57.9	71.2

[a] Concentrations of living ends. [b] Concentrations of chloromethyl groups. [c] Number-average molecular weight of recovered polymer. [d] Extent of coupling of living ends. [e] Extent of coupling of the chloromethyl groups which was estimated from the extent of coupling of living ends. [f] In THF. [g] In benzene.

in a mixture of benzene and tetrahydrofuran (THF) and characterized the resultant polymers by fractional precipitation. Yen[4] claimed that the use of potassium as the counterion instead of lithium was preferred to minimize side reactions in the anionic reaction with tetra(chloromethyl)benzene. Candau and Franta[7] have investigated the effects of some reaction conditions in the reaction of living polystyrene with chloromethylated polystyrene. Meunier and Van Leemput[5] prepared six-branched star polystyrene by using living polystyrene and hexa[p-(chloromethyl)phenyl]benzene. Recently, Ishizu et al.[9-12] reported the shielding effect of branches and the rate constant in the reaction of living polystyrene with chloromethylated polystyrene at low temperatures.

In previous studies, most of the reactions were carried out by treating the benzyl chloride groups with stoichiometric amounts or small excesses of living polystyrene, and the extent of the reaction was evaluated by characterizing the resultant polymer by fractional precipitation. This method is sensitive to intermolecular cross-linking, because the intermolecular cross-linking remarkably affects the evaluation of both the molecular weight and the amount of cross-linked polymer. Furthermore, fractional precipitation requires laborious work to obtain the desired results from a coupling reaction between living polystyrene and benzyl chloride groups. Perhaps because of these disadvantages, the effect of reaction conditions and investigation of the usefulness of the benzyl chloride group as an electrophilic coupler have not been studied in detail, although many papers have dealt with the coupling reaction. However, the method proposed in a previous paper[13] gives the number of coupled precursor molecules directly, leading to an easy evaluation of the extent of the polymer-coupling reaction. Thus, this method is suitable for the study of the coupling reaction making possible a novel approach to the reaction. By this method, we studied the coupling reaction between poly(chloromethylstyrene), P(CMS), and living polystyrene with special emphasis on the coupling reactivity of P(CMS) as a multifunctional backbone polymer and on the effect of reaction conditions. P(CMS) has the merit of possessing a well-defined structure as the backbone polymer compared with chloromethylatd polystyrenes which have randomly distributed chloromethyl groups.

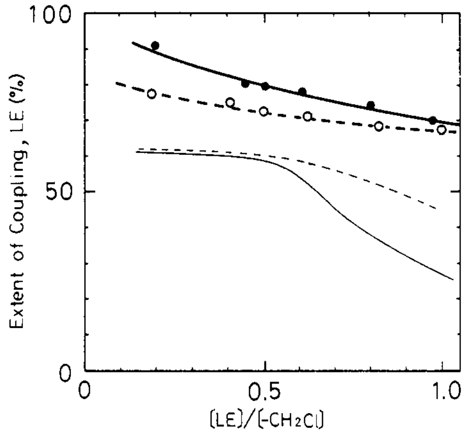

Figure 1. Relationship between the extent of coupling and the $[LE]/[CH_2Cl]$ ratio in the reactions of P(CMS) with PSt-K at 0 °C (●) and PSt-Li at 23 °C (○) and poly(p-vinylstyrene oxide)[1b] with PSt-K (—) and PSt-Li (- - -).

Experimental Section

Materials and Coupling Reaction. P(CMS) was prepared by radical polymerization of commercially available chloromethylstyrene (vinylbenzyl chloride: meta 60%, para 40% mixture; Tokyo Kasei Kogyo Co.) which was fractionally distilled just before the polymerization. The polymer was fractionated into five fractions by adding methanol to a 1% polymer solution in benzene at 30.0 °C. The third fraction was used as the backbone polymer for the coupling reaction and its number-average molecular weight was 6.34×10^4. The chlorine content of the backbone was found to be 22.1% (Calcd 23.2%) by elemental analysis. The NMR spectrum of the polymer contained resonances at $\delta = 7.0$ and at $\delta = 6.4$ (ppm) for the phenyl protons, at $\delta = 4.4$ for the chloromethyl protons, and at $\delta = 1.5$ for the methin and methylene protons. The ratio of the peak areas was 2:2:2:3. In the IR spectrum of the polymer, strong absorptions at 1265 cm^{-1} appeared corresponding to the chloromethyl group. The solution of P(CMS) for the coupling reaction was prepared in a high-vacuum system (10^{-5} mm Hg) as follows: the weighed P(CMS) was dissolved in a small amount of benzene which had been distilled in the presence of sodium–benzophenon. The solution was freeze-dried for 20 h, and the resulting residue was redissolved in a given volume of solvent (THF or benzene). PSt-Li and poly(styrylpotassium) (PSt-K) were prepared by the same method as described in the preceding paper.[1b] Their number-average molecular weights were 2.25×10^4 and 2.47×10^4,

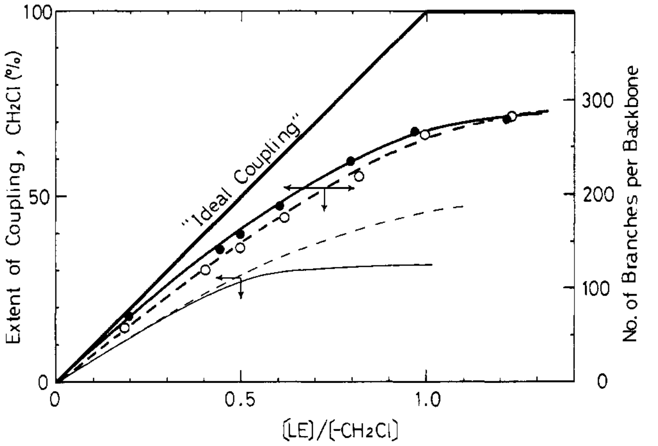

Figure 2. Relationship between the [LE]/[CH$_2$Cl] ratio and the extent of coupling of chloromethyl groups and number of branches per backbone polymer in the reactions of P(CMS) with PSt-K at 0 °C (●) and PSt-Li at 23 °C (○) and poly(p-vinylstyrene oxide)[1b] with PSt-K (—) and PSt-Li (- - -).

respectively. Solvents such as benzene and THF used for the coupling reaction were purified by methods appropriate for anionic polymerization experiments. Hexamethylphosphoric triamide (HMPA) and N,N,N',N'-tetramethylethylenediamine (TMEDA) were dried over calcium hydride and distilled in a high-vacuum system.

The reaction apparatus was the same as described in the preceding paper,[1b] and the experimental procedures were the same also. One prepolymer solution was added dropwise and slowly into the other over a period of about 8 h, however, in the investigation of the effect of the order of addition of the two prepolymers on the extent of coupling. The effects of reaction conditions on the extent of coupling were investigated by keeping the mole ratio of living ends to chloromethyl groups, [LE]/[CH$_2$Cl], at a constant value of 0.5.

Measurement and Evaluation of the Extent of Coupling. The determination of the number-average molecular weight and the turbidimetric titration were carried out in the same way as described in the preceding paper.[1b] Gel permeation chromatograms were measured in THF using a Spectra-Physics Model 3500B with a Shodex A-805 column or a Toyo Soda HLC-802UR with two GMH columns. The extent of coupling of living polystyrene was evaluated from the equation proposed in the previous paper.[13] The extent of coupling of chloromethyl groups in the backbone polymer was estimated from the value of the extent of coupling of the living polystyrene.

Results

Coupling Reactivity of the Prepolymers. The realtionship between the extent of coupling and [LE]/[CH$_2$Cl] ratio was studied. The results are given in Table I. When the value of [LE]/[CH$_2$Cl] was smaller than unity, the red or orange color of the living polystyrene completely disappeared, but slowly when the value of [LE]/[CH$_2$Cl] was large. When [LE]/[CH$_2$Cl] was larger than unity, the color did not disappear. As the value of [LE]/[CH$_2$Cl] increased, the extent of coupling of living polystyrene decreased whereas the extent of grafting of chloromethyl group increased. The extent of coupling of living polystyrene and chloromethyl groups was plotted against [LE]/[CH$_2$Cl] in Figures 1 and 2. In Figure 1, it can be seen that the extent of the coupling of living polystyrene with P(CMS) is higher than that[1b] with poly(p-vinylstyrene oxide). The extent of coupling of PSt-Li is less than that of PSt-K, but the reaction for the former was carried out at a higher temperature. In Figure 2, it can be assumed that the extent of coupling of chloromethyl group will be saturated at a value of [LE]/[CH$_2$Cl] more than 1.2.

Effect of the Reaction Conditions. Table II shows the effects of the addition of more polar solvents to the reaction medium. When a minute amount of THF was added to the P(CMS)–PSt-Li–benzene system, the extent of coupling decreased abruptly but then increased gradually as THF was added until its molar concentration exceeded 100 times that of living end. The extent of coupling actually became higher than that of the system with no THF when the molar concentration of THF exceeded about 1000 times that of living end. In the case of the addition of TMEDA to the same reaction system, the effect was slightly higher than that of THF. Even a small addition of HMPA increased the extent of coupling significantly whereas this effect was not seen in the reaction system of PSt-K and P(CMS) in THF.

The extent of coupling of both PSt-Li and PSt-K appeared to be higher at lower temperatures as shown in Figure 3. However, the rate of reaction slowed down at lower temperatures, e.g., the red color of the polystyryl anion did not disappear completely in the reaction of P(CMS) with PSt-K in THF at −78 °C even for 12 days (not included in Figure 3 because of incompletion of the reaction). The optimum tem-

Table II
Effect of Polar Solvents on the Coupling Reaction between Living Polystyrene and P(CMS) in Benzene[a]

Living PSt [LE] × 10^3, mol L^{-1}	P(CMS) [CH$_2$Cl] × 10^3, mol L^{-1}	[LE]/[CH$_2$Cl]	Polar solv, mol L^{-1}	[P. solv.]/[LE][b]	$(\overline{M}_n)_R$ × 10^{-4}	Extent of coupling of LE, %
PSt-Li			THF			
3.42	6.83	0.501	0	0	14.0	84.3
2.91	5.81	0.501	5.84	2.01	5.95	62.2
2.29	4.56	0.502	9.31	4.07	5.69	60.4
2.97	5.78	0.514	3.28 × 10	1.10 × 10	5.92	62.0
2.65	5.30	0.500	5.39 × 10	2.03 × 10	5.95	62.4
2.82	5.60	0.504	1.70 × 10^2	6.03 × 10	6.14	63.3
3.06	6.15	0.498	1.08 × 10^3	3.53 × 10^2	9.71	77.0
3.45	6.88	0.501	5.44 × 10^3	1.58 × 10^3	33.3	93.7
			TMEDA			
2.93	5.87	0.499	3.24 × 10	1.11 × 10	6.78	66.9
			HMPA			
2.94	5.87	0.501	3.25 × 10	1.11 × 10	36.4	94.3
2.97	5.93	0.501	3.32 × 10	1.12 × 10	41.8	95.1
PSt-K[c]						
2.68	5.36	0.500	3.02 × 10	1.13 × 10	12.0	79.7
3.11	6.21	0.501	0	0	11.9	79.5

[a] Reaction temperature, 0 °C. [b] Mole ratio of polar solvent to living end. [c] In THF.

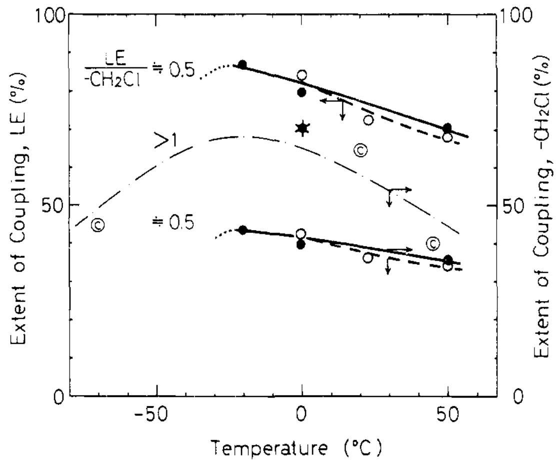

Figure 3. Dependence of the extent of coupling on the temperature in the reactions of P(CMS) with PSt-K (●) and PSt-Li (○). © denotes the data of Candau et al.[7] in the reaction of PSt-K with chloromethylated polystyrene. ✱ denotes the extent of coupling of the chloromethyl group in the reaction of P(CMS) with PSt-K at [LE]/[CH_2Cl] = 1.22.

perature is between −20 and −78 °C for the P(CMS)-PSt-K-THF system and is about 0 °C for the P(CMS)-PSt-Li-benzene system (seemingly in a super-cooled state).

Table III shows the effect of counterion. The extent of coupling is highly affected by the counterion, and the extent of coupling of the polystyryl anion is higher with Li^+ as counterion than with K^+ in THF–benzene medium.

Discussion

Comb-Shaped Polystyrene Obtained from P(CMS). Although P(CMS) contains a large number of pendant benzyl chloride groups which are close to each other, the backbone polymer showed an unexpectedly high extent of coupling with living polystyrene. Furthermore, the extent of intermolecular cross-linking seems to be negligibly small. This may be explained as follows. The polymer chain of P(CMS) used in this study has on the average 396 chloromethyl groups per molecule. Even if one out of 396 of the chloromethyl groups was utilized for intermolecular cross-linking in the equimolar reaction of chloromethyl groups of P(CMS) with living ends of living polystyrene, the resultant polymer would be expected to undergo gelation completely. However, the reactions of K-6 and L-6 have been observed to proceed homogeneously all the way, and the polymers recovered after the reactions were easily soluble in solvents which dissolve polystyrene. Therefore, the extent of intermolecular cross-linking must be negligibly small. Highly chloromethylated polystyrene would have a fairly large tendency[6] toward intermolecular cross-linking as it was reported that this reaction produced a large amount of polymer which had molecular weight higher than expected. Any measurable amount of micro-gel or super-macromolecules may be produced by an extremely small amount of intermolecular cross-linking as shown in the foregoing calculation.

From the viewpoint of preparation of well-defined polymer, Figures 1 and 2 may be referred to for finding the coupling efficiency of living polystyrene at various values of [LE]/CH_2Cl] and for controlling the number of branches per backbone, respectively. Furthermore, Figure 2 suggests that there is an upper limit to the number of branches per backbone. Figure 1 indicates that the coupling efficiency of living polystyrenes with P(CMS) is higher than that with poly(*p*-vinylstyrene oxide).[1b] However, the plots of the extent of coupling of living polystyrenes do not reach 100%. This fact does not suggest the incomplete reaction of living polystyrene but the occurrence of a side reaction besides the desired coupling, since the color ascribed to the living polystyrene completely disappeared when [LE]/[CH_2Cl] ratio was smaller than unity. The termination of living polystyrene seems not to be caused by impurities in a backbone polymer solution, because the extent of coupling is high at a small value of [LE]/[CH_2Cl].

With respect to possible side reactions, various reactions must be considered such as the metal–halogen interchange,[14] α-hydrogen abstraction,[15] one-electron transfer,[16] and carbene generation.[17] The study of the side reactions by means of model reactions is in progress and will appear in a later paper.

In order to ascertain the coupling reactivity of P(CMS) by another method, the gel permeation chromatograms (GPC) were measured of typical gross polymers obtained by C-1, K-3, K-6, and L-3. As shown in Figure 4, the respective GPC profiles have two peaks which are clearly identified as comb-shaped polystyrene and living polystyrene terminated without coupling with P(CMS). Since the amounts of backbone polymer used in these reactions are negligibly small (<1.5 wt %) in comparison with that of living polystyrene, the ratio of the area of the peak of the comb-shaped polystyrene to the total area of the two peaks may indicate the extent of coupling of living polystyrene. For C-1 and K-3, the extents of coupling evaluated by the GPC method are in good agreement with those calculated from the equation[13] which have been used in this paper. The high extent of coupling in the case of C-1 was verified. However, in the cases of K-6 and L-3 the extent of coupling by GPC method is somewhat lower than obtained by the equation. This discrepancy suggests the occurrence of a side reaction which is accompanied by the decrease in the number of polymer molecules. The relation between the discrepancy and the side reaction will be dealt with in a later paper. Figure 5 shows the GPC of the polymers of fractions I (comb-shaped polystyrene) and II (terminated living polystyrene) which were obtained by a single fractional precipitation of the gross polymer of K-3 according to the procedure described earlier.[1b] It can be seen that fraction I does not contain any of fraction II and vice versa. The peak of fraction I is symmetrical, which indicates the absence of intermolecular cross-linking of P(CMS). Moreover, the weight percentage of fraction I (78.7) is in good agreement with the extent of cou-

Table III
Effect of Counterion on the Coupling Reaction between Living Polystyrene and P(CMS)[a]

Expt	Counter-ion	Polyst. anion [LE] × 10^3, mol L^{-1}	P(CMS) [CH_2Cl] × 10^3, mol L^{-1}	[LE]/[CH_2Cl]	$(\overline{M}_n)_R$ × 10^{-4}	Extent of coupling of LE, %
C-1	Li^+	3.45	6.89	0.501	33.3	93.7
C-2	Li^+	3.46	6.86	0.504	30.6	93.1
C-3	K^+	3.04	6.09	0.499	12.0	79.8

[a] Solvent, benzene–THF (THF = 44 vol %); reaction temperature, 0 °C.

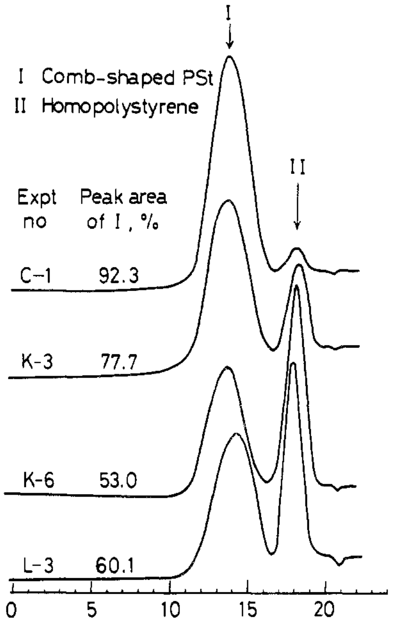

Figure 4. GPC profiles of the polymers obtained in C-1, K-3, L-3, and K-6.

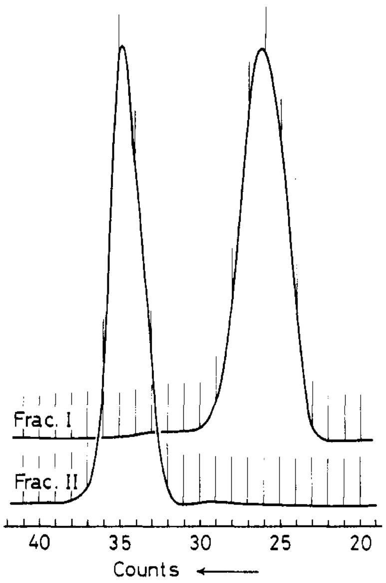

Figure 5. GPC profiles of fractions I and II in a single fractional precipitation of the polymer obtained in K-3.

pling of living polystyrene. Therefore, the separation of comb-shaped polystyrene from the gross polymer is easily done by fractional precipitation owing to the high coupling reactivity of P(CMS).

Various Conditions Affecting the Extent of Coupling. It has been reported[3,7] that the order of addition of prepolymer solutions is one of the reaction conditions which affects the extent of coupling in the reaction of living polystyrene with chloromethylated polystyrene. Therefore, we investigated the effect of order of the addition on the extent of coupling under conditions where $[LE]/[CH_2Cl] = 0.5$ (Table IV). A low degree of coupling was obtained when the backbone polymer solution was added to the living polystyrene solution while a high degree resulted in the reverse case. This finding agrees with the data of Candau and Franta.[7] This may be related to the fact that the extent of coupling of living polystyrene decreases with an increase in $[LE]/[CH_2Cl]$. The larger amount of living polystyrene would induce side reactions much more.

The extent of coupling suddenly drops when a minute amount of THF is added and then rises when the added amount of THF is increased as shown in Figure 6. This behavior seems to be similar to that of the propagation rate of PSt-Li in benzene[18] and THF–benzene mediums.[19] Therefore, the same concept of the form of active center established by the kinetic study of anionic polymerization can be applied to explain this phenomenon. The extent of coupling depends on the coupling reactivity of polystyryl anion in a PSt-Li dimer in benzene, or in a contact ion pair surrounded by THF molecules or a solvent-separated ion pair or a dissociated ion pair with Li^+ solvated by THF molecules with increasing addition of THF. The addition of a small amount of HMPA is fairly effective in comparison with THF. This may be due to the remarkable ability of HMPA for solvation with Li^+.

With regard to the reaction temperature, it has been reported that the displacement reaction was favored at elevated temperature.[2] However, as far as our experiments are concerned within the range of −20 to 50 °C, we observe that the extent of coupling was high at lower temperatures. Our result is in fairly good agreement with the dependence on temperature obtained by Candau and Franta[7] (Figure 3), supporting the postulate that at low temperature side reactions are suppressed.

Yen[4] claimed that K^+ was much better than Li^+ as a counterion for the coupling reaction, and many investigators have referred to this claim. Yen's claim was reasoned on the well-known metal–halogen interchange in the reaction of an organolithium compound with an organic halide and on the incomplete displacement ascribed to the covalent bond character of C-Li. However, the covalent bond character of C-Li should vary with the kind of the organolithium compound, e.g., PSt-Li, and poly(isopropenyllithiums) have greater ionic character than alkyllithiums because of the resonance stabilization of the carbanion. Furthermore, it is obvious from the kinetics[20] of the polymerization of styrene that ionic character of living polystyrene containing Li^+ is stronger than that containing K^+ when a large amount of THF

Table IV
Comparison of the Extent of Coupling in the Order of Addition of the Prepolymers[a]

Order of addition	Living PSt [LE] × 10³, mol L⁻¹	P(CMS) [CH₂Cl] × 10³, mol L⁻¹	[LE]/[CH₂Cl]	$(\overline{M}_n)_R \times 10^{-4}$	Extent of coupling of LE, %
PSt-Li into P(CMS)	3.38	6.92	0.488	8.35	73.2
P(CMS) into PSt-Li	3.31	7.08	0.468	6.13	63.3
PSt-K into P(CMS)	3.07	6.35	0.483	9.39	73.9
P(CMS) into PSt-K	3.10	6.23	0.498	7.04	65.0

[a] Reaction temperature, 23 °C.

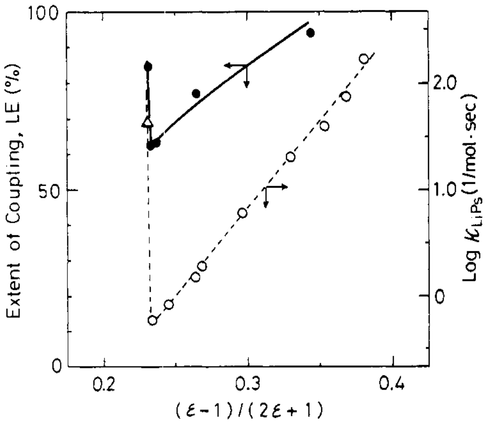

Figure 6. Comparison of the dependence of extent of coupling of living end on the dielectric constant (ϵ) which varies with the amount of added THF with that of the propagation rate constants of PSt-Li in similar mediums (○, data of Bywater and Worsfold[17]) and in benzene (△, datum of Roovers and Bywater[18]).

is present. In our experiments, it was found that Li^+ was more favorable than K^+ in a THF–benzene medium, as can be seen in Table III. This finding may be ascribed to the easy solvation of Li^+ with THF, which closely related to the ionic character of PSt-Li.

In conclusion, it may be noted that the solvent, the reaction temperature, and the counterion all affect the extent of coupling of living polystyrene, but the ionic character of the living polystyrene is the most important factor affecting the degree of the coupling.

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References and Notes

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Cross Relaxation in Poly(vinylidene fluoride) from Transient Overhauser Measurements

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ABSTRACT: Cross-relaxation effects between the ^1H and ^{19}F spin systems in poly(vinylidene fluoride) have been examined by the procedure devised by Solomon to study the HF molecule (transient Overhauser effect). The experiment has the virtue of providing unusually good resolution of T_1 components, determination of the cross-relaxation between two abundant spin systems, and an additional sampling frequency for molecular motions from a single pulse sequence.

In systems containing more than one magnetically resonant species, quantitative analysis of relaxation data requires a knowledge of competing cross-relaxation effects. Spin exchange between like nuclei spin diffusion has often been invoked in the interpretation of polymer relaxation data; exchange between unlike nuclei, though a highly improbable process in a rigid lattice, can evidently become important in the presence of thermal motion. Poly(vinylidine fluoride) (PVF_2) provides an interesting system from the standpoint of spin dynamics, molecular motion, and physical properties of practical importance.

In this paper we specifically examine spin exchange between proton and fluoride nuclei in PVF_2 by means of the transient Overhauser experiment.[1–4] These cross-relaxation effects have been hitherto neglected in existing interpretations of NMR experiments on PVF_2.[5]

Experimental Section

The pulse experiment described by Solomon[3,4] to study cross relaxation in anhydrous hydrofluoric acid has been employed here. Briefly, at $t = 0$, a 180° pulse is applied at the resonant frequency of the hydrogen spins (designated S in the Solomon notation) and the magnetization of the fluorine spins (designated I) is monitored by the application of a 90° pulse at subsequent times. The use of crossed coils, one tuned to fluorine resonance (30 MHz) and the other to proton resonance (31.888 MHz), constituted the principal modification to the basic spectrometer.[6] A Bruker pulse programmer provided the required pulse sequences and the use of a Nicolet computer coupled to the spectrometer via a Biomation 610 digitizer allowed the accumulation of signals. Owing to the cross-coil configuration the 180° pulse for the ^1H nuclei was 18 μs. However, we believe that substantially all of the magnetization is inverted by virtue of the following experiment carried out at room temperature. Application of an 18-μs 180° pulse, followed by an 8-μs delay and a 2-μs 90° pulse, shows an initial amplitude of the free induction signal of approximately 80%