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Triphase Catalysis. Influence of Percent Ring Substitution on Active-Site Mobility, Macroenvironment, Microenvironment, and Efficiency[1]

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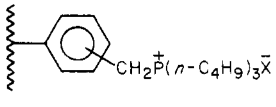
ABSTRACT: Microporous cross-linked polystyrenes (1% divinylbenzene) bearing methylenetri-*n*-butylphosphonium chloride (**1a**, 17% ring substitution (prs); **1b**, 52 prs) or mesylate groups (**2a**, 17 prs; **2b**, 52 prs) have been examined by ^{13}C NMR spectroscopy under triphase conditions. Pendant group mobility was high in **1a** and **2a** and was insensitive to the concentration of sodium chloride in the exterior aqueous layer; for **1b** and **2b** the mobility remained high but was inversely related to the salt concentration. Qualitatively, these results closely correlate with analysis made of the imbibed solvents; both show that (1) **1b** is physically responsive to changes in the salt concentration used whereas **1a** is not, (2) **1a** responds well to organic solvents and is insensitive to water, while the reverse is true for **1b**, and (3) when saturated sodium chloride solutions are used, pendant group mobility and polymer swelling are maximum under triphase conditions. Resins **1a** and **1b** have also been evaluated as triphase catalysts for chloride ion displacement on *n*-decyl methanesulfonate and for alkylation of β-naphthoxide by benzyl bromide. Over a wide range of salt concentrations, the amount of imbibed water in **1a** was low and nearly constant; its activity for chloride ion displacement was high and, within experimental error, constant. For **1b**, an increase in the salt concentration substantially decreased the water uptake and raised its activity. Whereas **1a** led to predominant O-alkylation of β-naphthoxide, **1b** afforded mostly C-alkylation.

Introduction

The precise relationship between macrostructure, microenvironment, and activity of polymer-based triphase catalysts is poorly understood.[3] Although kinetic studies have proven valuable in defining the synthetic utility of certain triphase reactions, they have provided little mechanistic insight. Recent attempts to rationally design new and more active catalysts have focused primarily on the nature of the catalytic site, where close analogy has been made to phase-transfer catalysis.[4] Little consideration, however, has been given to the *concentration* of these sites within the polymer.[5]

In the present work we closely examine the physical and chemical consequences of changing the active-site concentration in a typical triphase catalyst. For this purpose, we have selected polymers **1a**, **1b**, **2a**, and **2b**.[6,7] Our reason for choosing these polymers was fourfold. First, phosphonium-based resins are among the most active triphase catalysts.[7-10] Second, these polymers span the range of loadings which have been employed in most synthetic applications. Third, low cross-link densities provide maximum catalyst efficiencies;[7,8] they also afford reasonably narrow ^{13}C NMR line widths in solvent-swelled resins, making spectral analysis and evaluation of site mobility possible using conventional instrumentation.[11] Fourth, the mesylate ion in **2a** and **2b** allows for examination of ionically as well as covalently attached sites.



functionalized microporous
polystyrene–1% divinylbenzene
1a, 17% ring substitution;
X = Cl
b, 52% ring substitution;
X = Cl
2a, 17% ring substitution;
X = OSO$_2$CH$_3$
b, 52% ring substitution;
X = OSO$_2$CH$_3$

$C_6H_5CH_2\overset{+}{P}(n\text{-}C_4H_9)_3\overset{-}{X}$

3, X = Cl
4, X = OSO$_2$CH$_3$

Data which we now present from ^{13}C NMR, swelling, product distribution, and kinetic analysis show that the percent ring substitution has a substantial influence on the mobility, macroenvironment, microenvironment, and catalytic efficiency of tri-*n*-butylphosphonium groups attached to cross-linked polystyrene under triphase conditions.

Results and Discussion

^{13}C NMR Characterization. The procedures used for obtaining ^{13}C NMR spectra under biphase and triphase conditions were unexceptional and are described in the Experimental Section. Table I summarizes observed line widths, $\Delta\nu_{1/2}$, of the mesylate and pendant methyl carbons measured at full-width at half-height. These data provide direct information concerning the mobility of the active sites.[12] Also reported in this table are appropriate chemical shifts which reflect the microenvironment experienced by

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Table I

^{13}C NMR Chemical Shifts/Line Widths ($\delta/\Delta\nu_{1/2}$) of Phosphonium Salts[a]

	benzene		benzene–water		benzene–water plus NaCl[b]	water		water plus NaCl[b] CH_3
salt	Ms	CH_3	Ms	CH_3	CH_3	Ms	CH_3	
1a		13.99/15		13.99/10	13.99/8		/140[d]	
1b		/127		13.92/11	14.05/24		13.34/6[e]	13.59/41
3		13.60/2.9[c]					13.14/2.9[f]	
2a	40.60/40[g]	13.86/10	40.09/6[i]	13.86/7		39.50/29[j]	13.40/45	
2b	/60[g]	/61	40.02/7[i]	13.99/9		39.24/2[k]	13.27/5	
4	40.45/0.7[h]	13.56/1.8				39.21/1.5[h]	13.21/2.2	

[a] Chemical shifts (±0.07 ppm) and line widths (±2.0 Hz) for mesylate (Ms) and pendant methyl (CH_3) carbons. [b] Saturated sodium chloride. [c] 0.02 M benzene solution. [d] 1.5 mL of water. [e] 0.15 g in 2.5 mL of water. [f] 0.6 M aqueous solution. [g] 3.0 mL of solvent. [h] 0.9 M solution. [i] 3.0 mL of benzene plus 0.5 mL of water. [j] 2.0 mL of water. [k] 0.1 g plus 2.5 mL of water.

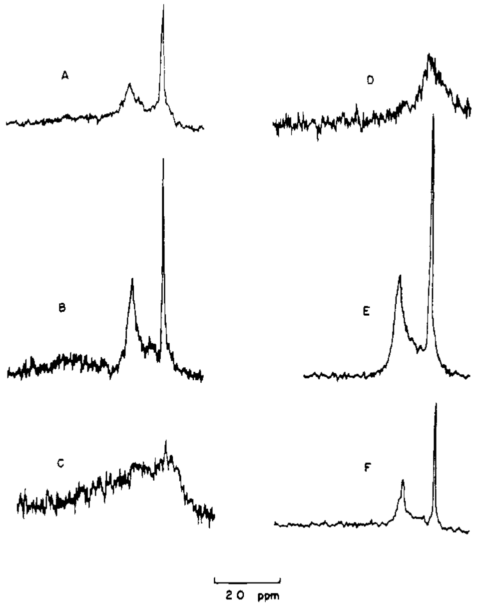


Figure 1. Aliphatic portion of the ^{13}C NMR spectra of (A) **1a** plus benzene, (B) **1a** plus benzene–water, (C) **1a** plus water, (D) **1b** plus benzene, (E) **1b** plus benzene–water, and (F) **1b** plus water.

these groups.[13] The aliphatic portion of the ^{13}C NMR spectrum of **1a** swollen in benzene, benzene–water, and water is shown in Figure 1. Only in the first two cases is the methyl resonance of the phosphonium group well resolved.[14] On the basis of a comparison of the integrated intensity of the methyl carbon (for **1a** swollen in benzene) with that of an internal standard (dioxane) and from similar measurements made for **3**, we estimate that all of the methyl groups contribute to the observed spectrum. The significant mobility of the pendant phosphonium groups in benzene-swollen **1a** is in sharp contrast to the water–**1a** system, where the entire aliphatic region is extensively broadened, indicating very restricted motion. When water plus benzene is employed, the resulting ^{13}C NMR spectrum is very similar to that produced with pure benzene; within experimental error, chemical shifts are identical. Interestingly, however, the line width is minimal under triphase conditions. The synergistic effect of water and benzene on promoting active-site mobility probably reflects hydration which reduces the clustering (physical cross-linking) and/or tightness of ion pairs within the polymer.[16] Similar results have been found for the mobility of both the mesylate and pendant methyl groups in **2a**. Finally, replacement of water by a saturated solution of sodium chloride produced no detectable change in the triphase spectrum of **1a**, showing that the mobility and microenvironment of the phosphonium groups are insensitive to the composition of the aqueous phase.

Polymers **1b** and **2b** have a much higher charge density than **1a** and **2a** and exhibit very different responses to identical swelling conditions. With benzene as the solvent, only very broad spectra were observed. In contrast, water produced relatively sharp resonances in which the mesylate and pendant methyl carbons were well resolved; chemical shifts and line widths were very similar to those of **3** and **4** in water, indicating mobile polymeric ions in an aqueous-like environment. When the combination of water plus benzene was used to swell **1b** and **2b**, the aliphatic region was very similar to that found with pure water as the solvent, except that the resonances were shifted downfield and the line widths were slightly increased. Replacement of water by a saturated sodium chloride solution in **1b** caused a further downfield displacement and increased line widths, indicating a responsiveness to the aqueous composition. Interestingly, when a saturated sodium chloride solution was used with **1b**, line widths were minimal under triphase conditions, reflecting a synergistic effect similar to that seen above for **1a**.

Imbibed Solvent Composition. On the basis of swelling procedures described by Gregor et al., we have developed a simple method for analyzing imbibed solvent compositions under triphase conditions.[17] A given weight of dry resin is equilibrated with the appropriate aqueous and organic solution followed by rapid suction filtration. The added weight of the polymer (D) represents the sum of the imbibed constituents. Extensive washing of the resin with ether and water, followed by analysis of the organic (GLC) and aqueous (titration) portions of the filtrate, yields the weight of imbibed toluene (A) and sodium chloride (B), respectively. The weight of adsorbed water (C) is obtained from the relationship, $C = D - A - B$. Detailed procedures are described in the Experimental Section. Table II summarizes all of the relevant data obtained for resins **1a** and **1b**. Duplicate measurements are also reported for several systems.

Under biphase conditions **1a** is moderately swollen by toluene and poorly swollen by water. Under triphase conditions, the amount of imbibed toluene remains unchanged but there is a substantial increase in water uptake. Incremental addition of sodium chloride to the aqueous layer caused no detectable change in toluene content under triphase conditions but did bring about a modest reduction in adsorbed water. In contrast to these results, **1b**, under biphase conditions, showed modest swelling in toluene and extensive swelling in water.[18] When subjected to triphase conditions, the imbibed toluene and water content were essentially unchanged. Furthermore, the amount of imbibed water in **1b** exhibited a substantial dependence on the concentration of sodium chloride. On going from pure water to a saturated sodium chloride solution, the amount

Table II
Imbibed Solvent Composition under Biphase and Triphase Conditions[a]

swelling conditions	1a NaCl, g	1a toluene, g	1a water, g	$10^5 k_{\mathrm{obsd}}$,[b] s^{-1}	1b NaCl, g	1b toluene, g	1b water, g	$10^5 k_{\mathrm{obsd}}$,[b] s^{-1}
toluene		0.62				0.35		
water			0.18				12.49	
water/toluene		0.57 (0.54)	0.81 (0.74)			0.43	11.91	
0.1 M NaCl	0.00		0.15		0.01		4.78	
0.1 M NaCl/toluene	0.00	0.53	0.73	4.6	0.01 (0.01)	0.36 (0.26)	4.47 (4.55)	0.7
1.0 M NaCl	0.01 (0.00)		0.15 (0.14)		0.04 (0.03)		2.21 (2.13)	
1.0 M NaCl/toluene	0.00	0.53	0.54	6.4	0.05 (0.04)	0.09 (0.09)	1.53 (1.58)	1.0
saturated NaCl	0.04		0.18		0.03		0.28	
saturated NaCl/toluene	0.13 (0.10)	0.56 (0.57)	0.46 (0.39)	5.8	0.02	0.37	0.44	4.1

[a] Per gram of dry resin; numbers in parentheses refer to duplicate experiments. [b] Pseudo-first-order rate constant for triphase displacement by chloride ion on n-decyl methanesulfonate.

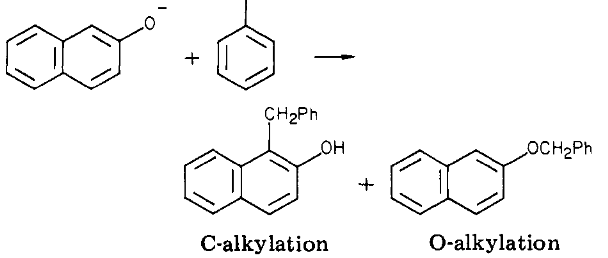
of water taken up by the resin decreased by a factor of 45 and 27 for biphase and triphase conditions, respectively. The amount of imbibed toluene was constant, except when a 1.0 M NaCl solution was employed. Here, the amount of toluene taken up by the polymer was surprisingly low.[19] Qualitatively, these swelling results closely correlate with those obtained from the NMR line width analysis. Both studies clearly show that **1b** is physically responsive, under triphase conditions, to changes in the salt concentration in the aqueous phase and that **1a** is not. They further show that **1a** responds well to organic solvents and is insensitive to water, while the reverse is true for **1b**. Finally, when saturated sodium chloride solutions are used, pendant group mobility correlates well with polymer swelling; both are maximum under triphase conditions.

Triphase Catalytic Activity. In addition to characterizing the active-site mobility and macroenvironment in **1a** and **1b**, we have also examined their triphase catalytic activity for chloride ion displacement on n-decyl methanesulfonate (eq 1).[8,10] Results presented in Table II show that catalyst activity is inversely related to the water

$$n\text{-}C_{10}H_{21}OSO_2CH_3(\text{org}) + \text{NaCl}(\text{aq}) \rightarrow n\text{-}C_{10}H_{21}Cl(\text{org}) + CH_3SO_3Na(\text{aq}) \quad (1)$$

content in the polymer. For **1a**, over a wide range of salt concentrations, the amount of imbibed water is low and nearly constant; its activity is high and, within experimental error, constant. For **1b**, an increase in the salt concentration substantially decreases the water uptake and raises its activity, which also shows that activity depends more on water content than on active-site mobility.

Oxygen vs. Carbon Alkylation. In order to probe the microenvironment within **1a** and **1b** under triphase conditions, we have measured the extent of O- vs. C-triphase alkylation of β-naphthoxide with benzyl bromide (eq 2).[20,21]



(2)

The product distribution of this reaction is known to be sensitive to the nature of the solvent used; i.e., O-alkylation is favored in dipolar aprotic solvents, while water promotes C-alkylation. Using **1a** as the catalyst, oxygen alkylation is predominant (94%); with **1b**, carbon alkylation is favored (81%). These results clearly demonstrate that there is a substantial difference in the microenvironment between these catalysts.[22]

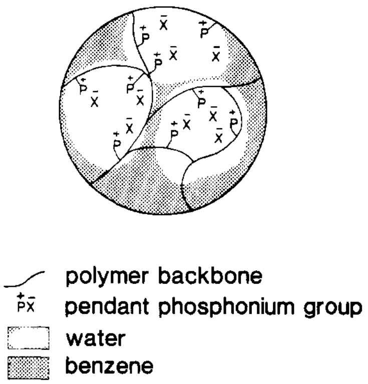


Figure 2. Schematic representation of **1a** (one bead) under triphase conditions.

Resin Microstructure. While the results presented in the previous sections do not unambiguously define resin microstructure, they do provide a basis from which reasonable speculation can be made. Under triphase conditions, **1b** is extensively solvated by pure water and partially solvated by toluene. This fact implies that the pendant ions are extensively hydrated and that the counterions are immersed in a "sea of water". Incremental addition of sodium chloride substantially reduces the water content of the polymer (osmotic shrinkage), creating "water pools".[23,24] In effect, this squeezes the counterions onto a hydrocarbon–water phase boundary.[25] Since the amount of imbibed toluene per gram of resin remains constant, the observed increase in catalytic activity that accompanies the decrease in water content probably reflects a higher effective concentration of chloride ion at the phase boundary and/or a more reactive ion. The high percentage of C-alkylation observed when **1b** was used as the catalyst clearly indicates that β-naphthoxide undergoes reaction in a protic environment and/or as an aggregated ion.[21,26,27] Considering that approximately one out of every two phenyl rings bears a phosphonium group, it is, in fact, difficult to imagine how these pendant ions could exist in a nonaggregated form.

Swelling data reported in Table II show that **1a** is capable of forming only "pools of water". It is reasonable, therefore, that this polymer exhibits little osmotic and catalytic response to changes in the salt concentration in the exterior aqueous phase. While the level of water uptake in **1a** is only moderate, it nonetheless, strongly suggests the presence of charge clustering.[28] Moreover, the marked preference for O-alkylation further indicates that the degree of aggregation is decreased and/or the extent of hydration is decreased vis-à-vis **1b**.

In Figure 2 we provide a schematic representation of what we fell best describes the microstructure of **1a** under triphase catalytic conditions. Here, pendant ions aggregate, forming inverted micelles which become encased in a polymer matrix. Resin **1b** is presumed to have a similar structure when high external salt concentrations are used, except that the ions are more highly aggregated. On the basis of analogy with micelle chemistry, we believe that chemical reaction occurs at or near a hydrocarbon–water phase boundary.[29] While further studies will undoubtedly strengthen or weaken our inverted-micelle view of ionic-based triphase catalysts, we feel it is an attractive model at this time.[30]

Experimental Section

General Methods. Resins **1a** and **2a** were prepared by quaternization of the corresponding chloromethylated copolymers with tri-*n*-butylphosphine, using established procedures.[5,9] Polymers **2a** and **2b** were prepared by reacting **1a** and **2a**, respectively, with excess *n*-decyl methanesulfonate in toluene at 100 °C as a two-phase process. Analysis of the liquid phase for 1-chlorodecane (GLC) and the resulting resin after washing (toluene) and drying [4 h, 80 °C (0.05 mm)] for chloride established that the exchange reaction was complete.[32] Benzene-d_6 was purchased from Aldrich Chemical Co. and used as obtained. Deionized water was distilled from $KMnO_4/Ba(OH)_2$. All ^{13}C NMR spectra were recorded with a JEOL FX 60Q (15.03 MHz) instrument operating in the Fourier transform mode at ambient temperature with complete proton decoupling. The spectral range, flip angle, and delay and acquisition times used were 4000 Hz, 30°, 250 μs, and 1.0 s, respectively. Polymers were measured by using 8K data points; monomers employed 16K data points. Oxygen degassing by bubbling nitrogen through the samples had no effect on spectral features. Imbibed toluene and product mixtures were analyzed by GLC on a Hewlett-Packard Model 5830 A flame ionization instrument.

NMR Sample Preparations. In a typical three-phase sample preparation, resin **1a** (1.0 g) was added directly to a 10-mm NMR tube followed by addition of 2.0 mL of benzene-d_6 which contained tetramethylsilane (Me_4Si) as an internal reference. With a 2-mL syringe equipped with a 6-in needle, 0.5 mL of deuterium oxide was introduced by injecting initially into the bottom of the gel and then slowly retracting the syringe from the NMR tube while injecting the remaining amount. The heterogeneous mixture was then stirred with a glass rod for 30 min. Resin beds extended 3–4 cm above the receiver coil. In water–resin and benzene–resin systems, the polymer/solvent ratio was adjusted to provide maximum swelling. For resin–liquid two-phase preparations, a given polymer was equilibrated with an excess of the appropriate aqueous or organic phase.

Triphase Catalytic Activity. Procedures used for evaluating the catalytic activity of **1a** and **1b** for the triphase displacement of chloride ion on *n*-decyl methanesulfonate were similar to those previously described.[5,9] In all cases 0.03 g of resin was used to catalyze the reaction of 0.375 mmol of the mesylate in 3 mL of toluene with 10 mL of an aqueous sodium chloride solution at 90 °C, using vigorous stirring. When a 0.1 M sodium chloride solution was used, kinetic runs were stopped before 20% conversion; other kinetic runs were carried out to 80%.

Imbibed Solvent Composition. The general procedure used for determining the imbibed solvent composition was as follows. A 50-mL Büchner funnel equipped with a fritted disk (70–100 μm) was weighed along with 1.0 g of dry resin. After adding an excess of toluene and/or aqueous solution, the mixture was stirred (glass rod) at 25 °C for 10 min and then left at room temperature for 1 h. The external liquid phase(s) was (were) removed under reduced pressure (water aspirator). Suction filtration was continued for 30 s beyond the point at which an external liquid phase could not be detected. This procedure was repeated at least two times to obtain a constant weight which represents the resin plus total imbibed constituents (D). Reproducibility of D was generally good (±5%). Immediately after the last measurement of D, the resin was washed with 50 mL of ether, containing 0.3 g of undecane (internal standard), followed by 75 mL of distilled water. The amount of toluene in the ether layer (A) was measured by GLC analysis, using a UC-W982 column. The aqueous layer was separated by means of a separatory funnel and diluted to 100 mL. An aliquot of the resulting solution (1 mL) was then titrated for chloride ion.[21] The total weight of sodium chloride was then calculated. The amount of adsorbed water (C) was calculated from the relationship, $C = D - A - B$.

In the O- vs. C-alkylation studies, where 0.5 M sodium naphthoxide was used in place of sodium chloride, the amount of imbibed salt was determined gravimetrically by weighing the residue of the filtrate after solvent removal. The amount of imbibed sodium naphthoxide in **1a** and **1b** was 0.20 and 0.06 g, respectively.

Triphase Alkylation of β-Naphthoxide with Benzyl Bromide. A standard triphase reaction was carried out as follows: An 8-mL culture tube (Corning no. 9826, 13 × 100 mm) equipped with a Teflon-lined screw cap was charged with 0.05 g of resin, 2.5 mL of a toluene solution containing 0.5 mmol of benzyl bromide plus 0.25 mmol of nonadecane (internal standard), and 3.0 mL of 0.5 M aqueous sodium β-naphthoxide. The tube was sealed and placed in an oil bath maintained at 50 ± 0.5 °C for 18 h. After cooling to room temperature, the aqueous layer was acidified by addition of 0.5 mL of concentrated HCl and the contents of the tube were quantiatively transferred to a 50-mL round-bottomed flask by repeated washing with methylene chloride (a total of 10 mL of CH_2Cl_2 was used). The organic layer was then analyzed directly by GLC on a Hewlett-Packard Model 5710 A flame ionization instrument (1.5 ft × 0.125 in UC-W982 on Chromosorb W column at 220 °C). Reactions were conducted as unstirred systems in order to avoid complexities due to a biphase component. Under the experimental conditions used, the total yield of alkylated product, based on benzyl bromide, using **1a** and **2a** was 69% and 36%, respectively. In the absence of catalyst, 0.5% of benzyl 2-naphthyl ether and 6% of 1-benzyl-2-naphthol were formed. Data reported in the text are corrected for this biphase component.

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Pyrolysis–Gas Chromatographic Studies on Head-to-Head Polystyrene

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ABSTRACT: Pyrolysis–gas chromatography (PGC) with a high-resolution glass capillary column was used in an investigation of head-to-head polystyrene (H–H PS). The peaks on the resulting pyrograms were identified by combining PGC–mass spectrometric results, retention data of the products, and pyrolysis–hydrogenation gas chromatographic results. On the basis of the resulting characteristic pyrograms, the thermal degradation behavior of H–H PS is discussed and compared with that for head-to-tail PS (H–T PS).

Vinyl-type polymers synthesized through usual polymerization reactions mostly consist of a head-to-tail (H–T) arrangement of the associated monomer units along the polymer chain. Therefore, stereoregularities and sequence distributions for the polymers have been mainly discussed by assuming only H–T linkages. On the other hand, it has been pointed out that minor amounts of irregular head-to-head (H–H) or tail-to-tail (T–T) linkages should affect the physical properties of the polymer.

So far, studies on the monomer arrangement have been most extensively carried out by IR and NMR spectroscopy. In addition to these, pyrolysis methods combined with either gas chromatography (PGC)[1-5] or mass spectrometry (PMS)[6] have been also demonstrated to be powerful techniques for the structural investigation of the polymers. Recently, PGC was effectively applied to the elucidation of the irregular monomer linkages in various highly alternating copolymers[3] and the estimation of the chemical inversions in polypropylenes.[5]

Recently, Fujimoto et al.[7] synthesized a model polystyrene (PS) consisting almost entirely of H–H linkages by a radical polymerization of 2,3-diphenyl-1,3-butadiene followed by selective reduction of the double bonds along the main chain with aniline and potassium metal. They studied its ^{1}H NMR spectrum and physical properties by light scattering, stress relaxation, and dilatometric methods and suggested that H–H PS should have a stiffer backbone than H–T PS. Later Inoue et al.[8] studied H–H PS synthesized through basically the same route as that used by Fujimoto et al.[7] and reported that H–H PS exhibited essentially the same glass transition temperature, T_g, and degradation temperature as those for H–T PS. The dilute-solution properties[9] and the detailed high-resolution ^{1}H and ^{13}C NMR spectra of H–H PS were also compared with those for H–T PS.[10] More recently, Lüderwald[6] studied the detailed thermal degradation behavior of H–H PS by the direct pyrolysis in a mass spectrometer (PMS) and reported that H–H PS yielded characteristic products such as stilbene and bibenzyl, which reflect the H–H structures of the polymer chain.

In this work, PGC with a high-resolution glass capillary column was used to characterize H–H and H–T PS. The peak assignment of the associated pyrograms was mostly carried out by combining the PGC–MS data and the retention data of the anticipated degradation products. Pyrolysis–hydrogenation gas chromatography was also utilized for peak confirmation. On the basis of the observed characteristic pyrograms, the degradation mecha-

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