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Pyrolysis Gas Chromatographic Characterization of Highly Alternating Copolymers Containing Styrene and Tetracyanoquinodimethan, Methyl Acrylate, Acrylonitrile, or Methyl Methacrylate Units

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ABSTRACT: A method of characterizing configurational microstructures of highly alternating copolymers was proposed using pyrolysis gas chromatography with a high-resolution glass capillary column. By this method, almost perfectly ordered microstructures of styrene (St)–tetracyanoquinodimethan (TCNQ) alternating copolymer were confirmed, and the degree of disordered configuration was estimated for various highly alternating copolymers such as St–methyl methacrylate (MA), St–acrylonitrile (AN), and St–methyl methacrylate (MMA) copolymers.

It is well known that highly alternating copolymers are obtained through copolymerization of electron-donor type monomers (unsaturated hydrocarbons, vinylamines, vinyl ethers, etc.) and electron-acceptor type monomers (acrylates, methacrylates, unsaturated nitriles, etc.) in the presence of monomer complexing Lewis acids such as $ZnCl_2$, $SnCl_4$, $AlEtCl_2$, etc. The copolymerization often proceeds spontaneously and yields highly alternating copolymers regardless of the monomer feed ratios. On the other hand, recently, Iwatsuki et al.[1] reported that tetracyanoquinodimethan (TCNQ), one of the most strong electron-acceptor reagents, copolymerized with styrene (St) spontaneously even at room temperature to yield an alternating copolymer without using any additional complexing reagents.

There have been many arguments about the polymerization mechanisms of the highly alternating copolymers. However, it is usually difficult to decide which view is definitely correct without knowing the detailed configurational microstructures of the resulting copolymers. So far, ^1H NMR and ^{13}C NMR were most frequently utilized for characterizing these microstructures.[1-8] The characteristic resonance peaks reflecting the disordered configurations, however, are often not so easy to assign positively, even if they are reasonably resolved among the strong cluster peaks reflecting the ordered configurations since the amount of the disordered configurations should be less than a few percent or so at most. Nevertheless, using high-resolution ^1H NMR (100, 220, or 300 MHz), Suzuki et al.[4] and Harwood et al.[5,6] suggested the existence of the disordered configurations to some extent in some so-called alternating copolymers.

In this work, therefore, a unique method of characterizing the microstructures of highly alternating copolymers was developed using pyrolysis gas chromatography (pyrolysis GC) with a high-resolution glass capillary column. By this method, the configurational microstructures of P(St-*alt*-TCNQ) were investigated, and the degree of disordered configurations was estimated for various highly alternating copolymers such as P(St-*alt*-MA), P(St-*alt*-AN), and P(St-*alt*-MMA).

Experimental Section

Materials. P(St-*alt*-TCNQ), which was synthesized in acetonitrile solution of St and TCNQ without using any additional complexing reagents at 40 °C,[1] was kindly supplied by Dr. S. Iwatsuki, Nagoya University. P(St-*alt*-MA), P(St-*alt*-AN), and P(St-*alt*-MMA), which were synthesized in the presence of a complexing reagent, $AlEt_{1.5}Cl_{1.5}$,[9] were kindly offered from Dr. M. Hirooka, Sumitomo Chemical Co. The associated homopolymers and random copolymers synthesized by the usual radical polymerization were also used as reference materials. Among them, a series of low conversion P(St-*co*-MA) samples[10] were kindly supplied by Dr. Y. Yamashita, Nagoya University.

Pyrolysis Gas Chromatographic Conditions. A vertical microfurnace type pyrolyzer, which was designed by the authors to attain instantaneous and specific thermal degradation of polymer samples,[11,12] was directly attached to a gas chromatograph, Shimadzu 7-AG, with a high-resolution glass capillary column (o.d. 0.9 mm × i.d. 0.3 mm × 50 m long) suspension-coated with OV-101 and Silanox (325 mesh) from Shimadzu. In order to get high resolution even for relatively polar components, the active sites of the inner surface of the glass capillary column were treated with a dilute solution of PEG-20M, baked out at 250 °C for 30 h by passing nitrogen carrier gas, and washed by chloroform prior to the final dynamic coating with OV-101. The column temperature was programmed from 50 to 250 °C at a rate of 4 °C/min; 55 mL/min of nitrogen flow at the pyrolyzer was reduced to 1.0 mL/min at the capillary column through a splitter (55:1). The dead volume of the splitter was packed with 5% of OV-101 on Diasolid H (80–100 mesh) of which temperature was maintained at 250 °C. Here, the packing in the splitter plays an important role for preventing column contamination by tarry components

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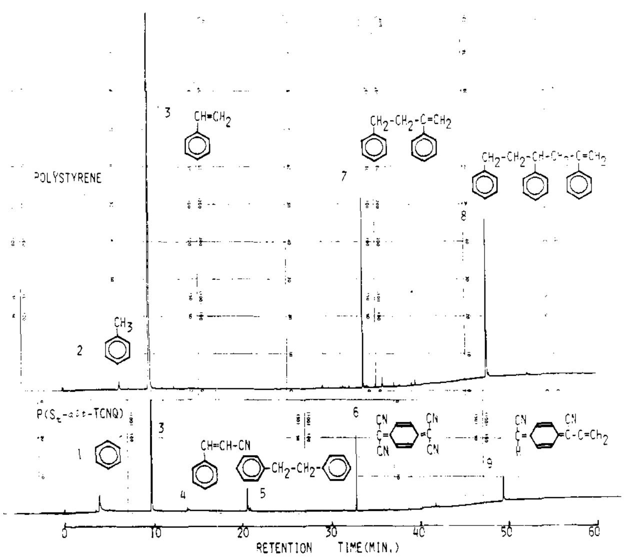
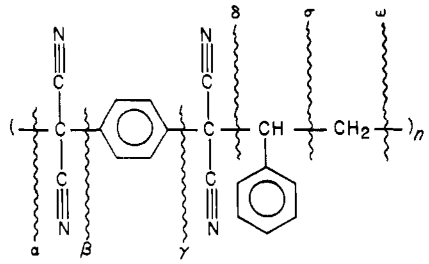


Figure 1. Pyrograms of P(St-*alt*-TCNQ) and PSt at 510 °C.

which results in a serious loss of resolution.[12] Samples ranging from 0.1 to 0.2 mg were pyrolyzed at 510 °C under a flow of nitrogen carrier gas. The peak area of the resulting pyrograms was integrated by an integrator, Chromatopack E-1A from Shimadzu, and the peak identification was carried out using a directly connected quadrupole mass spectrometer, JMS-Q10A from JEOLCO, which was operated in a chemical ionization mode.

Results and Discussion

P(St-*alt*-TCNQ). TCNQ copolymerizes spontaneously with a donor monomer such as St but does not undergo homopolymerization.[1] Therefore, Figure 1 shows only two pyrograms of P(St-*alt*-TCNQ) and the associated homopolymer, PSt, which was obtained through anionic polymerization. The main peaks of PSt at 510 °C are the monomer (mol wt = 104), dimer (mol wt = 208), and trimer (mol wt = 312) with the relative abundances 1.00, 0.11, and 0.14, respectively. On the other hand, on the pyrogram of the alternating copolymer, the peaks of St dimer and St trimer cannot be seen at all. The degradation products from the copolymer should be formed as follows:



The formation of benzene (peak 1) should mostly be attributed to β and γ scission followed by hydrogen transfer. Peaks 4, 5, and 9 should be the hybrid dimers formed by γ and α, β and σ, and α and ω scissions followed by partial elimination of CN groups and hydrogen transfer. Peaks 3 and 6 are due to the associated monomers formed by δ and ω and α and δ scissions, respectively. Comparison of these pyrograms suggests that only one unit of St surrounded by the counter monomer units is distributed along the copolymer chain, that is to say, the copolymer has almost perfectly alternating configurations of the monomer units.

P(St-*alt*-MA). Figure 2A,B shows the pyrograms of P(St-*alt*-MA) and P(St-*co*-MA) with a composition of St/MA = 49.7/50.3 which was synthesized by usual radical copolymerization in low conversion[10] and of which sequence distributions were investigated by PGC,[13] respectively. Although the main peaks of PSt and PMA are the monomers (S and M), the dimers (SS and MM), and the trimers (SSS and MMM), the copolymers yield the additional hybrid dimers (SM) and the hybrid trimers (SMM, MSM, SMS, and SSM). These hybrid products are not observed at all on the pyrograms of a physical blend of PSt and PMA under the pyrolysis conditions utilized. Here, MSM and SMS, for example, were distinguished from MMS and SSM, respectively, using fragmentation patterns of the corresponding mass spectra. In the following, all different peaks of MS with different carbon numbers and double bonds, for example, were assigned to one kind of MA-dimer after making correction for the molar sensitivity of each component in the flame ionization detector.[14] The peak assignments of the degradation products are basically the same as those described elsewhere.[13]

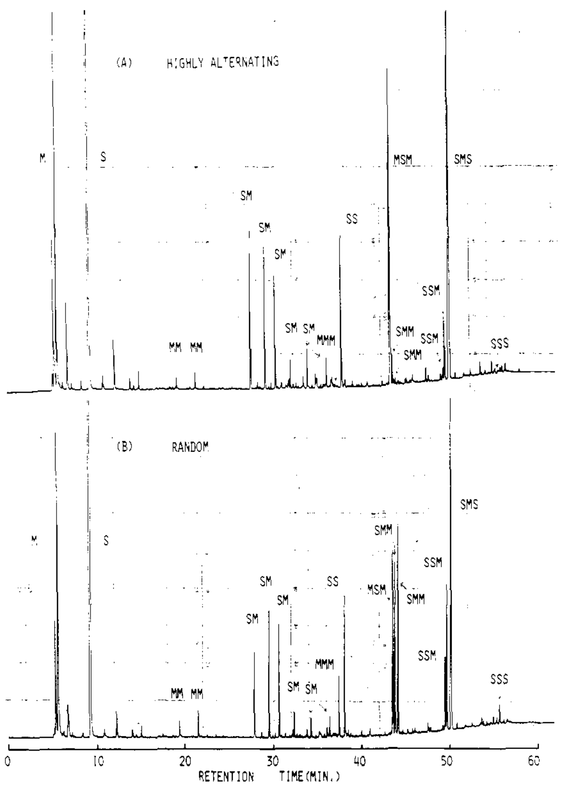


Figure 2. Pyrograms of St–MA copolymers at 510 °C: (A) P(St-*alt*-MA) with composition of St/MA = 50.2/49.8; (B) the P(St-*co*-MA) with composition of St/MA = 49.7/50.3. S is the St unit and M is the MA unit.

Table I summarizes the observed relative peak intensities (monomer unit ratio) for P(St-*alt*-MA) and P(St-*co*-MA) at the pyrolysis temperature of 510 °C. Qualitatively, a simple comparison of these pyrograms gives us clear information that the P(St-*alt*-MA) has highly alternating configurations since the pyrogram A has stronger peaks of SM, MSM, and SMS and smaller peaks of MM, MMM, SMM, SSM, and SSS than the pyrogram B does. However, it should be noticed that we can still see fairly strong peaks of SS and, though weak, peaks of MM, SMM, and SSM on the pyrogram A. These peaks should have disappeared on the pyrogram of a perfectly alternating copolymer. Here, the possibilities of the SS-dimer formation through the recombination of the St monomer produced in the microreactor can be denied by the following facts: (1) any SS dimer and SSS trimer are not observed by passing large quantity of St monomer through the reactor at 510 °C, and (2) the perfectly alternating

Table I
Relative Peak Intensity on the Pyrograms of St-MA Copolymers at 510 °C

peak assign	rel peak inten., I, % (monomer unit ratio) P(St-*alt*-MA)[a]	rel peak inten., I, % (monomer unit ratio) P(St-*co*-MA)[b]
M	31.12	24.59
S	31.13	34.33
MM	1.17	1.86
SM	9.23	7.50
SS	2.20	2.09
MMM		2.61
MSM	10.16	5.62
SMM	0.56	7.49
SSM	1.23	4.21
SMS	13.05	8.95
SSS	0.15	0.39
total	100.00	100.00

[a] Composition of St/MA = 50.2/49.8. [b] Composition of St/MA = 50.2/49.8.

copolymer, P(St-*alt*-TCNQ),[1] does not yield any SS dimer nor SSS trimer under the same pyrolysis conditions.

The relatively strong peak of SS dimer from the highly alternating copolymer is reasonably explained as follows. The SS diad which happens to exist in the highly alternating copolymer is most likely surrounded by the counter monomer units to form ∿MSSM∿. However, as can be seen in the following experimental data observed with a series of low conversion random copolymers, P(St-*co*-MA) with different compositions,[10,13] the isolated SS diad in the copolymer chain most likely yields SS dimer during the thermal degradation. Figure 3 shows relationships between dimer formation constants, k_{d1} (= P_2(SS)Y_2(SS)), k_{d2} (= (P_2(MS) + P_2(SM))/Y_2(SM)), and k_{d3} (= P_2(MM)/Y_2(MM)), and relative P_4(MSSM) concentration, r (= P_4(MSSM)/(P_4(MSSM) + 2P_4(MSSS) + P_4(SSSS)), where P_2(SS), P_4(SSSS), and Y_2(SS), for example, are the concentrations of SS diad and SSSS tetrad in the copolymer chain and the observed relative SS dimer yield at 510 °C, respectively.

Although the values of k_{d2} and k_{d3} are almost constant (about 1) regardless of the sequence distributions in the copolymers, that of k_d monotonously changes as a function of the r value. For example, the line extrapolation in Figure 3 predicts $k_{d1} \doteqdot 0.05$ and $k_{d2} \doteqdot k_{d3} \doteqdot 1$ for a hypothetical highly alternating copolymer with $r = 0.95$. These data suggest that for the isolated SS diad in the copolymer chain, ∿MSSM∿, which is the most similar case to the SS diad in P(St-*alt*-MA), the St units are liberated as SS dimer with about 20 times higher probability than they are liberated as SM-hybrid dimer together with the neighboring MA units. Therefore, the SS diad, if any, in the highly alternating copolymer, fairly preferentially appears on the pyrograms as SS dimer. On the other hand, the two successive units of MA in the highly alternating copolymer most probably take a structure, ∿SMMS∿, and should have almost equal probabilities to yield SM and MM-dimers since k_{d2} and k_{d3} have almost comparable values. Moreover, the St units in the St-MA copolymers almost quantitatively appear on the resulting pyrograms as peaks of S, SM, SS, SMM, MSM, SSM, SMS, or SSS, while about 95% of the MA units are recovered on the pyrograms as the associated peaks such as M, SM, SMM, MSM, SSM, SMS, and MMM.

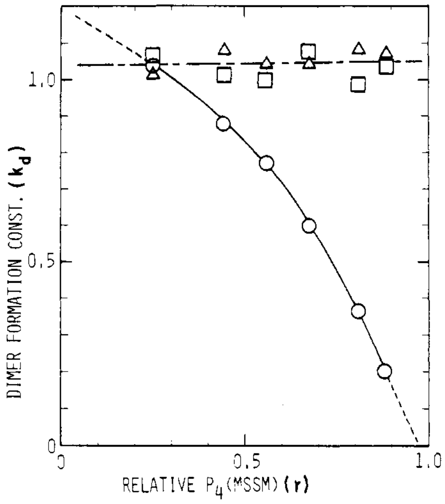


Figure 3. Relationships between dimer formation constants, k_d, and relative P_4(MSSM) concentrations, r: (○): k_{d1} = P_2(SS)/Y_2(SS); (△) k_{d2} = (P_2(SM) + P_2(MS))/Y_2(SM); (□) k_{d3} = P_2(MM)/Y_2(MM); r = P_4(MSSM)/(P_4(MSSM) + 2P_4(MSSS) + P_4(SSSS)).

Therefore, using the relative peak intensities of I_{SS}, I_{SSM}, and I_{SSS} which are associated with long sequences of the St unit (Table I), we can estimate the minimum degree of disordered configurations (DDC) in the highly alternating copolymer as follows:

$$\mathrm{DDC}(\%) = 2\left(\tfrac{1}{1} I_{SS} + \tfrac{1}{2} I_{SSM} + \tfrac{2}{2} I_{SSS}\right) = 2\left(2.20 + \tfrac{1}{2}1.23 + \tfrac{2}{2}0.15\right) = 5.93 \quad (1)$$

where $^1/_1$, $^1/_2$, and $^2/_2$ are the ratios of the disordered diad among the possible combinations. The value of the effective peak intensity was multiplied by a factor of 2 since about equivalent disordered configurations of MA units could be expected to exist in the highly alternating copolymer with the composition St/MA ≑ 50/50. Thus the DDC was estimated as 5.93% for the P(St-*alt*-MA). In this calculation, however, the possibilities of the formation of St monomer from the structures such as ∿MSSM∿ and ∿MSSSM∿ were neglected. Therefore, the actual DDC in the copolymer could be a little bit higher than 5.93%.

Table II
Relationships between Triad Concentrations and Trimer Yields from St-MA Copolymers at 510 °C

combination of monomers	P(St-*co*-MA)[a] $P_3(\cdots)$[b]	P(St-*co*-MA)[a] $Y_3(\cdots)$[c]	P(St-*co*-MA)[a] k_t (= Y_3/P_3)[d]	P(St-*alt*-MA)[a] $Y_3(\cdots)$[c]	P(St-*alt*-MA)[a] $P_3(\cdots)$[e]
MMM	0.040	0.089	2.2		
MMS + SMM	0.203	0.256	1.26	0.022	0.017
MSM	0.255	0.192	0.753	0.404	0.539
SMS	0.256	0.306	1.20	0.519	0.432
MSS + SSM	0.205	0.144	0.702	0.049	0.070
SSS	0.041	0.013	0.32	0.006	0.019
total	1.000	1.000		1.000	1.077

[a] The compositions are the same as those in Table I. [b] Calculated from the usual copolymerization theory. [c] Observed relative trimer yield ($\Sigma Y_3(\cdots) = 1.000$). [d] Apparent triad concentrations from $Y_3(\cdots)/k_t$.

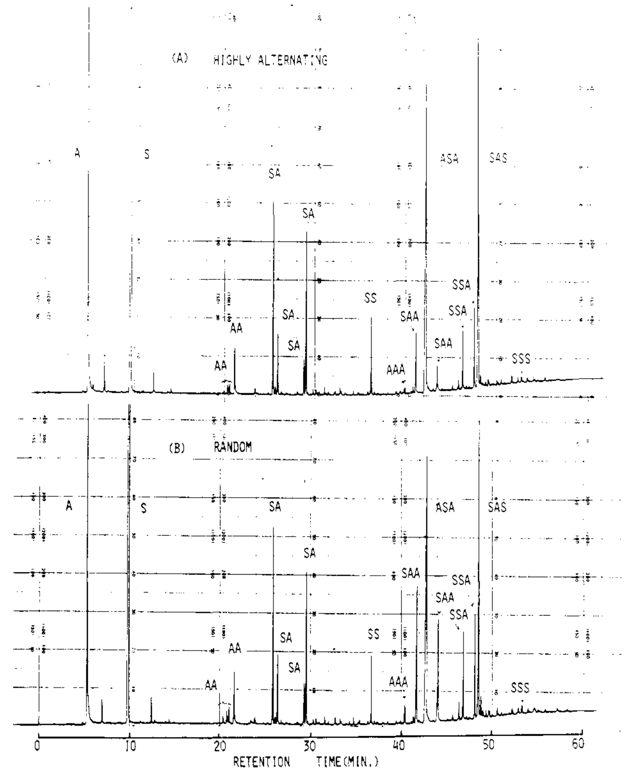


Figure 4. Pyrograms of St–AN copolymers at 510 °C: (A) P(St-*alt*-AN) with composition of St/AN = 51.1/48.9; (B) P-(St-*co*-AN) with composition of St/AN = 50.4/49.6. S is the St unit and A is the AN unit.

An alternative estimation of DDC can be made by using apparent trimer formation constant, k_t, observed with the random P(St-*co*-MA). Table II summarizes the data of the triads, $P_3(\cdots)$, and the observed relative trimer yields, $Y_3(\cdots)$, for the copolymers. From the relative concentrations of $P_3(\mathrm{MMS}) + P_3(\mathrm{SMM})$, $P_3(\mathrm{MSS}) + P_3(\mathrm{SSM})$, and $P_3(\mathrm{SSS})$, which are estimated for the P(St-*alt*-MA) using a relation of $P_3(\cdots) = Y_3(\cdots)/K_t$, the value of DDC can be calculated as follows:

$$\mathrm{DDC}(\%) = [1/2(\overline{P_3(\mathrm{MMS}) + P_3(\mathrm{SMM}) + P_3(\mathrm{MSS}) + P_3(\mathrm{SSM})}) + P_3(\mathrm{SSS})/\Sigma P_3(\cdots) \times 100 = \frac{\frac{1}{2}(0.017 + 0.070) + 0.019}{1.077} \times 100 = 5.80\% \quad (2)$$

where the factor of $^1/_2$ was used for MMS + SMM and MSS + SSM since half of each triad is associated with disordered diad. The reasonably close values of DDC, 5.93 and 5.80, would support the validity of the assumptions implicit in this method.

P(St-*alt*-AN). Figure 4A,B shows the pyrograms of P(St-*alt*-AN) and P(St-*co*-AN) with composition of St/AN = 50.4/49.6 which was synthesized by an usual radical copolymerization in low conversion. Since the P(St-*co*-AN) itself has fairly high alternating configurations because of the small value of $r_{\mathrm{St}}r_{\mathrm{AN}} = 0.0164$, the apparent pyrograms for both copolymers around the cluster of the dimer peaks are very similar to each other. The trimer peaks of ASA and SAS, however, are fairly strong on the pyrogram A. Applying the first method mentioned in eq 1, the DDC for the P(St-*alt*-AN) can be estimated as 6.8%, while the value obtained using the apparent trimer formation constant, k_t, defined in Table II, becomes 6.9%. In these calculations, the contribution of a large amount of the pyrolysis residue (about 20% of the original polymer sample) was neglected by assuming that the characteristic peaks that appeared on the pyrogram reflect the average microstructures of the copolymer sample.

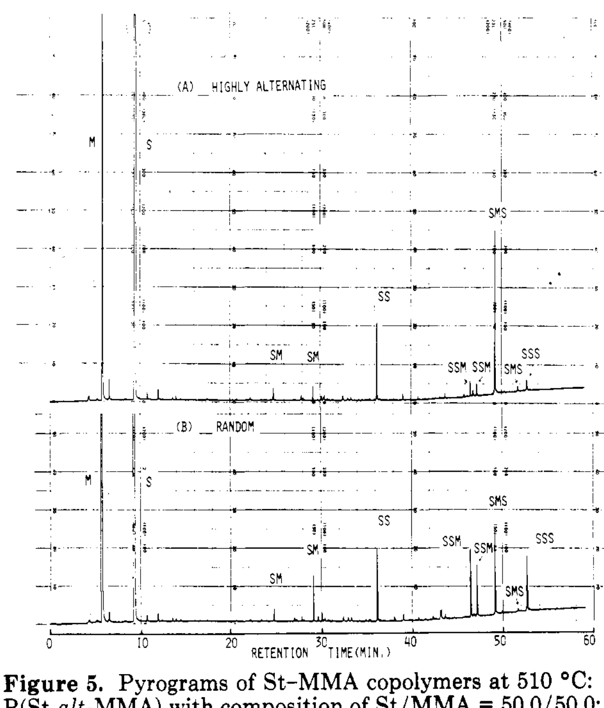


Figure 5. Pyrograms of St–MMA copolymers at 510 °C: (A) P(St-*alt*-MMA) with composition of St/MMA = 50.0/50.0; (B) P(St-*co*-MMA) with composition of St/MMA = 50.1/49.9. S is the St unit and M is the MMA unit.

Table III
Estimated Degree of Disordered Configuration in Highly Alternating Copolymers

copolymers	DDC, %
P(St-*alt*-TCNQ)	0
P(St-*alt*-MA)	5.9, 5.8
P(St-*alt*-AN)	6.8, 6.9
P(St-*alt*-MMA)	4.0

P(St-*alt*-MMA). Although PMMA has a tendency to depolymerize completely into the monomer at elevated temperatures around 500 °C, the St–MMA copolymers yield some hybrid dimers and trimers in addition to the main peaks of St and MMA monomers. Figure 5A,B shows the pyrograms of P(St-*alt*-MMA) and P(St-*co*-MMA) with a composition of St/MMA = 50.1/49.9. On these pyrograms, in addition to the monomers (S and M), the peaks of SM, SS, SMS, SSM, and SSS can be seen, while those of MM, MMM, SMM, and MSM are missing. Therefore, the method utilizing the apparent trimer formation constants, k_t, cannot be applied to this copolymerization system. However, in this case, both monomer units in the copolymer samples appear on the resulting pyrograms almost quantitatively. So, applying the first method mentioned in eq 1, the minimum value of DDC was estimated as 4.0% for the P(St-*alt*-MMA).

Table III summarizes the estimated values of DDC in the highly alternating copolymers. Although the recovered fraction of the original sample on the corresponding pyrogram slightly changes depending on the nature of the copolymer, namely 98.0, 97.5, and 84.0% for P(St-*alt*-MMA), P(St-*alt*-MA), and P(St-*alt*-AN), respectively, the reproducibility of the pyrogram measurement was quite satisfactory. For example, as for P(St-*alt*-MMA), the coefficients of variance for seven repeated measurements of the absolute monomer yields are 3.37 and 3.54% for St and MMA, respectively. Further, as for the relative peak intensity for the monomers, St/MMA, the coefficient of variance amounts to only 0.45%.

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Separation of Styrene–Methyl Acrylate Copolymer According to Chemical Composition, Using High-Speed Liquid Chromatography

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ABSTRACT: It was shown that copolymer samples can be separated according to their chemical compositions by high-speed liquid chromatography (high-speed LC) and also that high-speed LC is hopeful for the rapid and automatic determination of chemical composition distribution (CCD) of copolymers. The chromatograms of a mixture of styrene–methyl acrylate copolymer samples having sharp CCD and different chemical compositions, respectively, were obtained using columns packed with silica gel particles whose micropore size is smaller than about 50 Å by the gradient-elution method with a mixed solvent (CCl_4/methyl acetate). The chromatograms showed discrete peaks corresponding to the original components. The apparent CCD of a component was determined from the chromatogram using the respective components as inner standards and compared with the theoretical CCD calculated from copolymerization kinetics. The CCD obtained by using a higher efficiency column was in fairly good agreement with the theoretical one. Moreover, it was shown that the molecular sieve effect is negligible in the present columns.

It is no doubt important for the study of copolymers to establish a rapid and automatic method for the determination of chemical composition distribution (CCD) of copolymers, such as gel permeation chromatography in the determination of molecular weight distribution. Several methods have been proposed for the determination of CCD. Among them, cross fractionation[1-4] and thin-layer chromatography (TLC)[5,6] can give quantitative results. However, the former is very laborious, and the latter cannot be operated automatically.

Four mechanisms of separation participate in high-speed liquid chromatography (high-speed LC), which is a powerful, rapid, and automatic method for separation or characterization of chemical compounds, follow: (1) adsorption–desorption, (2) partition, (3) molecular sieve, and (4) ion exchange. Despite the fact that in the characterization of low molecular weight compounds all of these are utilized, in the characterization of high polymers, only mechanism 3 is used in gel-permeation chromatography. In TLC of high polymers, on the other hand, not only mechanism 3 but also mechanism 1 are used.[7] The separation of copolymers according to their chemical compositions[5,8-14] and the determination of CCD[5,6] were successfully carried out in TLC based on mechanism 1. Therefore, if high-speed LC can be operated based on mechanism 1, adsorption–desorption, high-speed LC may be hopeful for the rapid and automatic determination of CCD of copolymers.

It is the purpose of the present work to show that copolymer samples can successfully be separated according to their chemical compositions by high-speed LC and also that the rapid and automatic determination of CCD of copolymers by high-speed LC is promising. Mixtures of copolymer samples with different chemical compositions were eluted out with a mixed solvent whose composition was changed linearly with time (gradient-elution method) and separated into the original components.

Table I
$\overline{M}_n$ and MA Content of Copolymers

sample	$\overline{M}_n \times 10^{-5\,a}$	MA content, mol %[b]
N-45(w)[c]	2.61	46.6
F-1	4.38	(46.6)
F-4	2.92	(46.6)
F-7	1.40	(46.6)
N-60(w)[c]	2.76	57.3
F-1	6.36	(57.3)
F-4	3.68	(57.3)
F-7	1.62	(57.3)
N-75(w)[c]	3.02	77.9

[a] Osmometry. [b] Elemental analysis (see Experimental Section). [c] Whole copolymer.

Experimental Section

Materials. Whole polymers and their fractions of styrene–methyl acrylate (St–MA) random copolymer were used in the present work. Their preparation, fractionation, and characterization methods were presented elsewhere.[15] These copolymer samples may have narrow CCD because of their low conversions. The MA content of the whole copolymer was determined by elemental analysis. The MA content of the fraction was not measured directly, but its refractive index increment, measured by differential refractometer, was equal to that of the whole

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