Table III
Variations Observed in Gelation Reactions and Products[a]

solvent	benzene	benzene/THF (0.994/0.006)	dioxane/toluene (0.750/0.250)
time to full color, s	>120	instantaneous	instantaneous
time to gel,[b] s	~1200	~20	~160
expected overall rate constant,[c] L mol^{-1} s^{-1}	0.01	25.3[d]	0.9
clarity of gel	opaque	clear	clear
structural characteristics of gel	inhomogeneous (powder)	homogeneous (swollen rubber)	homogeneous (swollen rubber)

[a] Experimental conditions are as in Table I, keeping the relative volume of solvent constant. [b] Subject to small deviations due to an inability to accurately control reaction temperature. [c] Based on values for lithium polystyryl (from ref 5). [d] Assuming propagation is via monoetherate of lithium polystyryl (from ref 5).

unassociated contact ion pairs.[5] Therefore by carrying out a gelation in this solvent, we have maintained the same addition mechanism as for the case of reaction in pure benzene solvent, while essentially eliminating living-end association. The 25% toluene was added to the dioxane in order to obtain a solubility parameter comparable to that of benzene while having the dielectric characteristics of the solvent mixture for the most part unchanged from that of pure dioxane. The results of these experiments appear in Table III along with analogous information from the previous two solvent systems. The clarity and structural characteristics of the dioxane/toluene and benzene/THF gels were indistinguishable. The gelation times for the three cases are consistent with the reported values for the rates of polymerization of styrene in the respective solvents (Table III). This supports our earlier assumption regarding the similarity in reaction mechanism between styrene and divinylbenzene in each system.

In the case of dimeric lithium poly(divinylbenzyl), as found in benzene without THF, the proximity of the terminal pendent vinyl group of one living chain to the active end of its associated counterpart greatly enhances the probability of interchain reaction. Such reaction essentially doubles the molecular weight and the "living" functionality of the resulting species. Successive dimerization and cross-linking of separate species quickly increases the molecular weight, cross-link density, and "living" functionality of the growing polymer, which all lead to microsyneresis. Adding THF to benzene or using dioxane–toluene eliminates lithium poly(divinylbenzyl) dimerization. In the absence of such association early stage polymerization is expected to be predominantly linear chain growth due to the high concentration of monomer units relative to polymer repeat units. Linear polymerization is also enhanced by a factor of 2 for the vinyl content of DVB monomer compared to polymer repeat unit and by the inability of ethylstyrene to contribute to cross-linking. Prior to gelation, the reaction medium is composed of soluble living polymer which then forms a macroscopic homogeneous network.

The termination-free nature of this polymerization and high ceiling temperature ensure virtually complete incorporation of monomer into the gel. We have also observed that the gelation reaction stops at the point of swelling equilibrium; i.e., the "living" gel does not undergo macrosyneresis[1] nor does the recovered product swell further in excess solvent. Future work will be aimed at clarifying this phenomenon, the kinetics of the homogeneous gelation reactions, and the detailed structural features of the products.

Conclusions

A method has been presented for preparing homogeneous gels of divinylbenzene–ethylstyrene which contain a significant concentration of pendant vinyl groups. Microsyneresis is avoided by adding a suitable amount of THF to the reaction medium, thereby eliminating unwanted living-end association.

The utility of these gels has been demonstrated for the particular case of purification of solvent. Numerous other applications can be envisioned which exploit the variety of organic and organometallic reactions to which the pendant vinyl group is susceptible, e.g., use as a catalyst substrate.

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Carbon-13 Nuclear Magnetic Resonance Spectra of Alternating and Random Copolymers of Methyl Acrylate with Styrene

H. KOINUMA,* T. TANABE, and H. HIRAI

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan. *Received September 30, 1980*

In spite of the wide applicability of NMR spectroscopy for structural elucidation of polymers, spectral patterns of copolymers are frequently too complicated, owing to both configurational (tacticity) and compositional (monomer sequence) distributions, to provide us with quantitative information concerning the microstructure. Recently we showed that the alternating copolymer could

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Table I
^{13}C Chemical Shifts of PSt, PMA, and P(MA-*co*-St)s[a]

polymer	C=O	aromatic			OCH$_3$	CH	CH$_2$
		C$_1$	C$_2$,C$_3$	C$_6$			
polystyrene		145-146	128.0	125.6		40.7	43-44
poly(methyl acrylate)	174.8				51.7	41.3	34.9
alternating copolymer	175.9	142.5-143.2	128.2 127.6	126.3	51.1	41.6 41.0	~39
random copolymer	175.9 175.4 174.9	143-144	128.2 127.6	126.2	51.1 ~51.6	41.2	~43[b] ~39 ~35[c]

[a] In deuteriochloroform, at 33 °C; ppm from Me$_4$Si (chemical shifts with respect to the internal Me$_4$Si reference). [b] Observed in styrene-rich copolymers. [c] Observed in methyl acrylate-rich copolymers.

Table II
Relative Intensities of Split Peaks of the Carbonyl Carbon Resonance and the Calculated Sequence Distribution in P(MA-*co*-St)

copolymerization conditions	f_M,[a] %	relative intensity[b]			sequence content[c]		
		peak 1	peak 2	peak 3	[SMS]	[MMS]	[MMM]
SnCl$_4$, -10 °C	50.0	~1.0	~0	~0	0.53	0.40	0.07
ZnCl$_2$, 4 °C	50.8	~1.0	~0	~0	0.55	0.38	0.07
BPO, 60 °C	47.2	0.56	0.37	0.07	0.56	0.38	0.07
BPO, 60 °C	66.1	0.21	0.51	0.28	0.21	0.50	0.29

[a] Molar fraction of MA in P(MA-*co*-St). [b] Chemical shifts for peaks 1-3 are 175.9, 175.4, and 174.9 ppm, respectively, from internal Me$_4$Si standard. [c] Calculated by using the following equations: [SMS] = P_{MS}^2, [SMM] = $2P_{MS}(1 - P_{MS})$, [MMM] = $(1 - P_{MS})^2$, and $P_{MS} = 1/(1 + r_{MA}x)$, where S and M are St and MA units, r_{MA} is the reactivity ratio of MA (0.18), and x is the ratio of MA to St in the feed.

conveniently be used for the analysis of ^{13}C NMR spectra of methyl methacrylate (MMA)–styrene (St) copolymers.[1] This result solved the problem of the contradicting assignments previously reported by two different groups[2,3] for the cotacticity-dependent splittings.

Concerning the microstructure of methyl acrylate (MA)–St copolymers, there is only a limited amount of information from IR[4] and ^{1}H NMR[5] studies. In this note, we describe the characteristic ^{13}C NMR spectral patterns observed for MA–St copolymers at 25.03 MHz.

Results and Discussion

Figure 1 shows 25.03-MHz ^{13}C NMR spectra of two kinds of equimolar copolymers of MA and St, one prepared in the presence of stannic chloride at −10 °C under UV irradiation and the other in the presence of benzoyl peroxide at 60 °C. The assignment given in Figure 1 and also in Table I is based on the comparison of chemical shifts with those of PMA and PSt as well as on the partially decoupled spectra. In the ^{1}H NMR spectrum, the former copolymer shows a splitting into an approximate 1:2:1 triplet in the methoxyl region. Since the splitting was attributed to triad cotacticity,[5,6] the copolymer should have an atactic stereosequence. Thus, the apparent singlet pattern in the carbonyl region in Figure 1a does not indicate a stereospecific structure of the copolymer. These results can reasonably be interpreted by the idea that the copolymer has a uniform, presumably alternating, sequence structure and that its ^{13}C NMR is insensitive, at least under the present measuring conditions, to the configurational variation (i.e., cotacticity) of the copolymer chain. An equimolar copolymer prepared in the presence of zinc chloride has a ^{13}C NMR spectrum almost identical with the one shown in Figure 1a, the result being consistent with the generally accepted notion that alternating copolymers of polar vinyl monomers with electron-donating monomers are prepared when metal halides are used as complexing agents. Even if the alternating sequence structure is considered, the ^{13}C NMR spectrum of the MA–St copolymer is far simpler than those of other vinyl copolymers such as acrylonitrile–α-methylstyrene,[7] methacrylonitrile–α-methylstyrene,[8] and methyl methacrylate–styrene.[3] Cotacticity contributes to spectral complication as for these latter copolymers. In compensation for the inability to know the cotacticity, this simplicity in the ^{13}C NMR spectrum of MA–St copolymers can provide an advantage for the determination of sequence distribution in random copolymers, as described below.

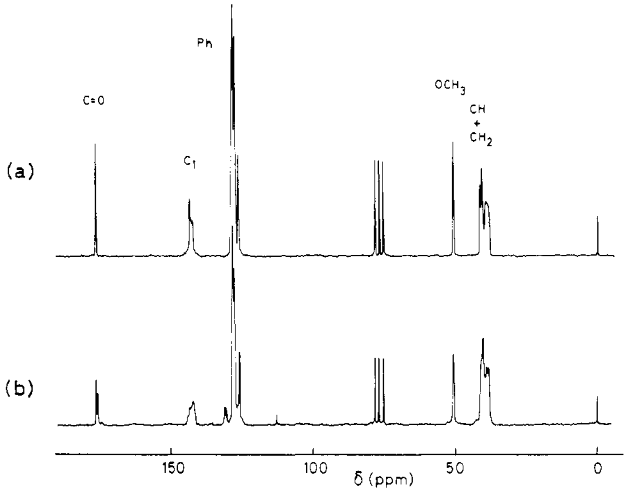

Figure 1. Proton noise decoupled, natural-abundance ^{13}C NMR spectra of methyl acrylate (MA)–styrene (St) equimolar copolymers (in CDCl$_3$ at 25.03 MHz and 33 °C). (a) Copolymer prepared in the presence of SnCl$_4$ (f_M:MA content = 50.5 mol %). (b) Random copolymer initiated with benzoyl peroxide (f_M = 47.2 mol %).

An almost equimolar random copolymer of MA with St has the ^{13}C NMR spectrum shown in Figure 1b. The carbonyl carbon region of the expanded spectrum is depicted in Figure 2, together with the same regions of the spectra of the alternating copolymer and of PMA. Chemical shift values for all these copolymers and for PSt are listed in Table I. From the comparison of chemical shifts, the triply split peaks at 175.9, 175.4, and 174.9 ppm for the carbonyl carbon in the random copolymer can be assigned to SMS, MMS (SMM), and MMM triad sequences

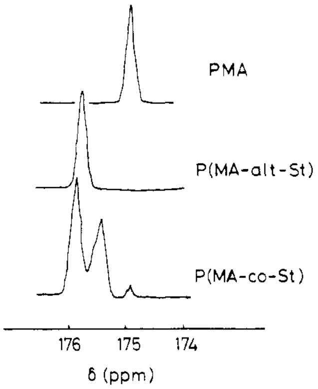

Figure 2. Carbonyl carbon part of ^{13}C NMR spectra of PMA, P(MA-*alt*-St), and a random copolymer (f_M = 47.2 mol %).

from lower magnetic field, where M and S denote, respectively, MA and St units. Inversion–recovery measurements revealed that the ^{13}C species corresponding to these three carbonyl peaks had the same spin–lattice relaxation time, 2.4 s, when measured in 10 w/v % $CDCl_3$ solution at 33 °C. Further, the relative intensities of these triplet peaks were confirmed to be in good agreement with the contents of the above triad sequences calculated on the conventional radical copolymerization mechanism. This direct correlation between the relative intensities of triplet carbonyl carbon resonance and the sequential triad contents calculated hold generally for random MA–St copolymers with various compositions. Representative data are given in Table II. Thus, the distribution of triad monomer sequences in MA–St copolymers can be quantitatively and easily determined from the split peaks of the carbonyl carbon resonance.

The NMR signals of the other carbons in the copolymer provide little information about the microstructure. The equimolar copolymer obtained in the presence of metal halides showed a singlet at 39.2 ppm, the chemical shift just in the middle between those for the methylene carbons in PMA (34.9 ppm) and in PSt (43–44 ppm, broad). This equivalence of the two methylene carbons, one originating from MA and the other from a St unit, should also be attributed to the alternating sequence structure. In addition to this singlet, which is assigned to the methylene carbon in the MA–St dyad and which is not affected by cotacticity, two methylene signals of MA–MA and St–St dyads appear in the spectra of random copolymers at the same positions as for the methylenes in PMA and PSt, respectively. However, the partial overlapping of these signals with the signals at 40–42 ppm due to the methine carbons in both monomer units makes it difficult to measure the dyad sequence distribution with adequate reliability.

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Products of Oxidation of Styrene

FRANK R. MAYO* and R. E. CAIS

SRI International, Menlo Park, California 94025, and
Bell Laboratories, Murray Hill, New Jersey 07974.
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This note integrates the results of a paper by Mayo[1] (designated by M, often with section numbers) and one by Cais and Bovey[2] (designated by C&B, often with page numbers) on the products of oxidation of styrene. It shows that most of the differences in the conclusions in the two papers are associated with the different oxygen pressures used and the products taken for study. The C&B work is based on ^{13}C NMR studies of poly(styrene peroxides) made at 15 and 760 torr of oxygen and then precipitated several times from benzene with methanol. Thus the 55% yields of benzaldehyde and styrene oxide that M-4.1 reported at 15 torr and the methanol-soluble polymer were neglected. M-2.2 analyzed the whole polymers, mostly by C and H with O by difference but sometimes also by peroxide determinations (M-2.7), although both methods have limitations. Benzaldehyde and styrene oxide were determined separately. M carried out oxidations at 50 °C and oxygen pressures from 0.19 to 3200 torr. C&B determined the structures of their two copolymers by ^{13}C NMR.

Excess Methylene Groups

From several lines of evidence, M-2.7 and -4.5 concluded that copolymers made at the lowest oxygen pressures contained methylene groups left from incomplete decomposition of polyperoxide into benzaldehyde and formaldehyde. The H/C ratio in styrene and its polyperoxide is 1.000; in $C_8H_8 + CH_2$ and its polyperoxides it is 1.111. The best evidence for excess methylene groups in styrene polyperoxide is the H/C ratio of 1.07_9 in M-Table II for the polymer made at 1.1 torr of oxygen. The 1.03_6 ratios in copolymers made at 15 and 740 torr suggest excess methylene groups but this discrepancy is not well beyond experimental error. Further evidence for methylene groups comes from M-4.5 and M-Table II. These show that two copolymers contained peroxide groups that did not give benzaldehyde on pyrolysis. However, the evidence for $-CH_2-O-$ groups in poly(α-methylstyrene peroxide) made at low pressure (M-8.5) is compelling; although polymers made at high and low oxygen pressures have nearly the same C:H:O ratios, the former is a polyperoxide but the latter is not; it apparently contains $-C_9H_{10}-O-$ and $-CH_2-O-$ groups. C&B are confident that $-O-CH_2-O-$ groups were absent in their 15-torr copolymer but are less confident about the absence of $-CH_2-CHPh-CH_2-O_2-$ groups. We conclude that the proportion of excess methylene groups is low and uncertain in the 15-torr polymer but becomes significant at lower pressures.

Further, there is a discrepancy between the M and C&B copolymers made at 15 torr when their compositions are expressed on the same basis. The M copolymer contained 1.18 C_8H_8/O_2 (counting two ether links as one peroxide link) and contained 73.2% C. From the chain composition of the C&B polymer on p 173, the C_8H_8/O_2 ratio is 1.38_3, corresponding to 75.49% C, which is significantly different from the M value. An elemental analysis of the C&B copolymer is desirable to support their conclusions. The difference between the two copolymers may be the result

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* To whom correspondence should be addressed at SRI International.

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