Synthesis of methacrylic acid–styrene block copolymers by living radical polymerization in the presence of chitosan

Seiichi Kataoka and Tadanao Ando

Government Industrial Research Institute, Osaka, 8–31 Midorigaoka 1-chome, Ikeda 563, Japan

The existence of living growing end radicals in the radical polymerization of sodium methacrylate (MAA·Na) in the presence of chitosan acetate salt has been ascertained by preparing block copolymers with styrene as secondary comonomer. When polymerization of MAA·Na eventually reached 93.4% conversion after 144 h at 30°C, secondary comonomer styrene added to the system undergoes further polymerization. Solvent extraction was performed to separate the homopolymers and block copolymers in order to determine the properties of the product. The results of the solubilities, of gel permeation chromatography and of ^{1}H nuclear magnetic resonance showed the characteristics of the block copolymers.

INTRODUCTION

It is known that a growing end radical is generally accompanied by a termination and transfer reaction but the possibility of living radical polymerization has been studied recently. There are two methods of stabilizing the growing end radicals and of controlling the approach of the end radicals. Examples of the former include a stabilized radical in perfluoro-2,5-diazahexane-2,5-dioxyl and a living copolymerization of hexafluoropropylene[1]. The production of living growing end radicals by the latter is limited to the specific polymerization system, e.g. heterogeneous polymerization system[2], emulsion polymerization system[3], clathrate polymerization system[4], high polymer association polymerization system[5], and coordination radical polymerization system[6].

Sorbic acid in chitosan (1) solution[7] and sodium methacrylate (MAA·Na) in chitosan acetate salt (2) solution[8,9] initiate the radical polymerization through stereoregularity. The polymers produced were confirmed to be optically active. It was estimated that those acidic

monomers were polymerized in such a way that they combined with the molecules of (1) and (2) by a coulombic force, and in addition by hydrophobic interaction between nonpolar groups of (1) and methyl groups of monomer molecules. It was found that the molecular weight of the poly(methyacrylic acid) produced by living radical polymerization in the presence of (2) increases with the conversion[10] and depends upon molecular weight of (1) used as a template, that is, molecular weight regulation takes place in it[11].

In the present paper, we have studied the production of the block copolymer by the addition of styrene as a secondary comonomer in order to confirm the existence of stable active radicals in the growing chains of MAA·Na polymer in the presence of (2) in the radical polymerization.

EXPERIMENTAL

Reagent

Preparation of (1): The sample described in the previous report[10] was used. The content of the amino group in (1) was 99.5 mol%, determined by the colloid titration method. The number-average molecular weight of (1), calculated from g.p.c., was 202 000 (number average of polymerization of degree of 1253 as glucosamine unit).

Methacrylic acid and styrene were purified according to classical procedures. Acetic acid, potassium persulphate (KPS) and water were purified according to the methods used in the previous report[10]. MAA·Na was prepared from methacrylic acid and sodium hydroxide at pH 7.0.

Block copolymerization

The block copolymerization was carried out in the

(1)

(2)
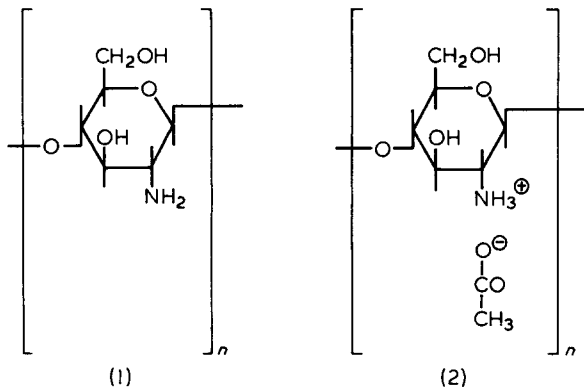
sealed glass tube shown in *Figure 1*. The mixture of (2) solution (added to acetic acid having a molar equivalent to (1)) and MAA·Na solution was put into part A, styrene and water into part B and a specified amount of KPS as an initiator into part A. After the polymerization was carried out at 30°C for 144 h, further polymerization was continued for a specified time after the addition of styrene through cock C. Acetic acid was directly added to this polymerization system to make a 20% acetic acid solution. After sodium nitrite was added to bring about hydrolysis of (1), dialysis was carried out in distilled water in a dialysis tube (made by Visking Co.). The solution was concentrated in an evaporator at reduced pressure and then lyophilized to obtain a copolymerization product (6). The conversion was determined gravimetrically. The methyl ester (7) was prepared by esterification of the copolymer (6) with diazomethane.
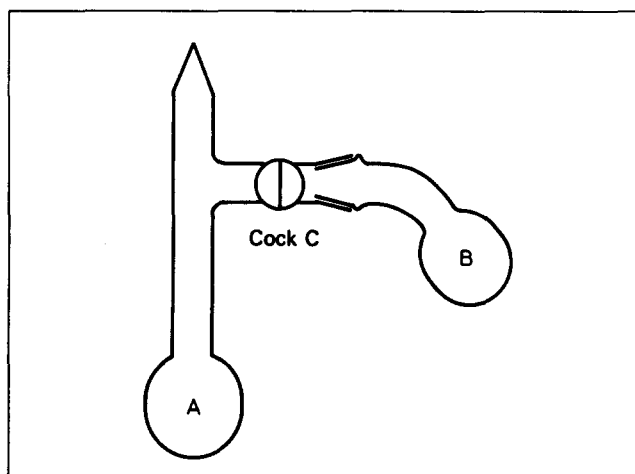

Figure 1 Glass apparatus for polymerization

Measurement

The intrinsic viscosity was determined at 25°C using an Ubbelohde viscosimeter. Chloroform was used as the solvent. Infra-red spectra were obtained using an IR-G spectrometer of Nippon Bunko Co. ^{1}H n.m.r. spectra of (7) were measured on a JNM-PS-100, 100 MHz spectrometer of Nippon Denshi Industry Co. in deuterochloroform solution with an internal standard (TMS). G.p.c. of (7) was recorded on a Waters HLG-6000A equipped with four columns (μ-styragel; $10^5 + 10^4 + 10^3 + 10^2$ Å). THF was used as an eluent and the flow rate was set at

Scheme 1

1.0 ml min^{-1}. The molecular weight of (7) was determined according to the calibration curve obtained with standard polystyrene. The fractionation of the copolymer (6) was carried out using a Soxhlet extractor.
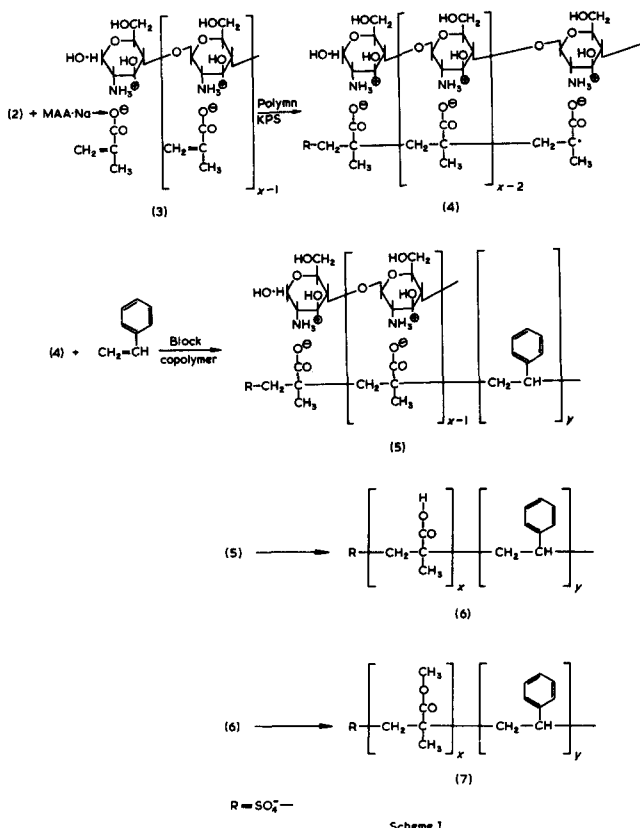
RESULTS AND DISCUSSION

The preparation method of the block copolymer is shown in Scheme 1. The polymerization conditions were as follows: [(2)] (base mole) = [MAA·Na] = 8.12 × 10^{-2} mol 1^{-1}, [KPS] = 8.86 × 10^{-4} mol 1^{-1}. Block copolymerization was then carried out in such a way that the polymer segment was copolymerized with styrene. Even when styrene was added to MAA·Na in equivalent moles, it was uniformly dispersed in the polymerization system.

The polymerization system of (2) and MAA·Na was uniform in the beginning, but began to become cloudy after several hours, and then the insoluble matter was deposited as the polymerization proceeded. When the molar ratio of the amino groups of (2) to MAA·Na was 1.0 in the polymerization system, the molecular weight of poly(methacrylic acid) produced increased in linear proportion to the increase of the conversion and finally the conversion attained 93.4% in 144 h, wherein the number-average molecular weight calculated from the peak shown in the g.p.c. curves was 11.5 × 10^4. In our earlier studies on the polymerization of MAA·Na in the presence of (2), it was proposed that an initiation reaction occurred at the reducing end-group of (1), and the propagation reaction proceeded among methacrylate molecules bound on molecule (1) by the ionic and hydrophobic binding[10].

The time–conversion curve for the block copolymerization of MAA·Na with styrene in (2) is shown in *Figure 2*. It reveals that the polymerization of MAA·Na in (2) terminates when most of the MAA·Na has been consumed, and that the conversion of styrene increases with time, when styrene is added to the polymerization system for secondary polymerization. The growing end radicals are still living in the polymerization system.

The conversion and the composition of the copolymer (6) produced by the secondary polymerization of the polymer segment of the (2)–MAA·Na system with styrene are shown in *Table 1*. It reveals that the conversion, the intrinsic viscosity and the styrene content of the copolymer (6) increase with time.
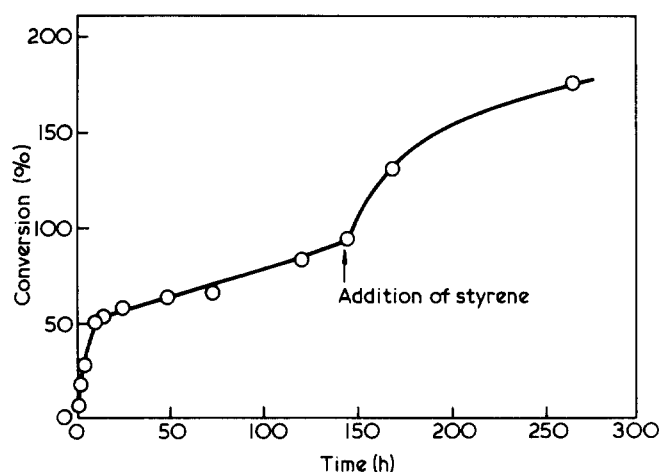
The copolymer (6) produced is composed of a methacrylic acid unit and a styrene unit. It is known that homopoly(methacrylic acid) does not dissolve in benzene but does so in methanol, while homopolystyrene does not dissolve in methanol but does so in benzene. The fractio-

nation of the copolymer (6) (run no. A-2 in *Table 1*) was carried out by the benzene–methanol system in a Soxhlet extractor. The extraction procedure is shown in *Figure 3*. The copolymer (6) was extracted by benzene for 24 h to separate the soluble portion (6A) from the insoluble portion, which was extracted by methanol for 24 h to separate the soluble fraction (6B) from insoluble fraction (6C). Methyl esterification (7) of these separated fractions of the copolymer (6) was carried out to investigate their characteristics. The styrene content of these methyl esterified fractions (7) was determined by ^1H n.m.r., except for fraction (7A) which was determined by i.r. The results of the fractionation are shown in *Table 2*. The copolymer (6) was separated into three fractions by the extraction method as mentioned above.

The efficiency of fractionation is illustrated by the g.p.c. curves shown in *Figure 4*. The g.p.c. curve of the unfractionated (7) shows two peaks, the main peak of which is positioned on the higher molecular weight side, representing the styrene content to have a mole fraction of 0.45. The g.p.c. curve of fraction (7A) shows only one peak, representing the extraction rate to be 10% and the styrene content to have a mole fraction of 0.92. Both g.p.c. curves of fraction (7B) and (7C) show two peaks each. The main peak of fraction (7B) is positioned on the lower molecular weight side, the extraction rate is 23% and the styrene content has a mole fraction of 0.27; the main peak of fraction (7C) is positioned on the higher molecular weight side, the extraction rate is 67% and the styrene content has

Figure 3 Fractionation of the block copolymers

Table 2 Fractionation of (MAA–styrene) block copolymer[a]

Fraction	Extraction ratio (wt%)	$[\eta]$[b] (dl l^{-1})	Mole fraction[c] of styrene unit in copolymer
Unfractionated	–	1.17	0.45
6A	9.9	1.49	0.92[d]
6B	23.2	0.44	0.27
6C	66.9	1.38	0.45

[a] Extraction time 24 h
[b] In chloroform at 25°C
[c] Determined by ^1H n.m.r. analysis
[d] Determined by i.r. analysis

a mole fraction of 0.45. The main peak of fraction (7C) has a higher molecular weight than that of the starting living poly(methyl methacrylate) (*Figure 4*).

As mentioned above, the g.p.c. curve of unfractionated (7) shows two peaks. It is considered that the polymer segment of the (2)–MAA·Na system is not uniformly copolymerized with styrene in water in the secondary polymerization. The two peaks in the g.p.c. curves of fraction (7B) and (7C) are considered to be caused by the difference in the solubilities of these polymers in methanol because they have different styrene contents. The trapped radicals of poly(acrylonitrile) and poly(vinyl chloride) are polymerized with styrene to give a block copolymer. Since the solubility changes remarkably by this block copolymerization with styrene, it is reported that the copolymer also dissolves into the solvents for polystyrene[2].

The ^1H n.m.r. spectrum of fraction (7C) is shown in *Figure 5*. A phenyl proton in each styrene unit gives two peaks at 7.1 δ and 6.5 δ, while a methoxy proton in each methyl methacrylate unit gives a peak at 3.6 δ. An α-methyl proton in each methyl methacrylate unit does not

Figure 2 Time-conversion curve for living radical polymerization of MAA·Na in the presence of (2) and block copolymerization with styrene at 30°C. [(2)] = [MAA·Na] = 8.12 × 10^{-2} mol l^{-1}, [KPS] = 8.86 × 10^{-4} mol l^{-1}, [styrene] = 8.12 × 10^{-2} mol l^{-1}, in water

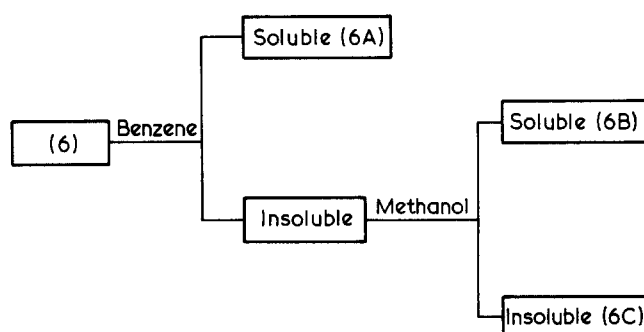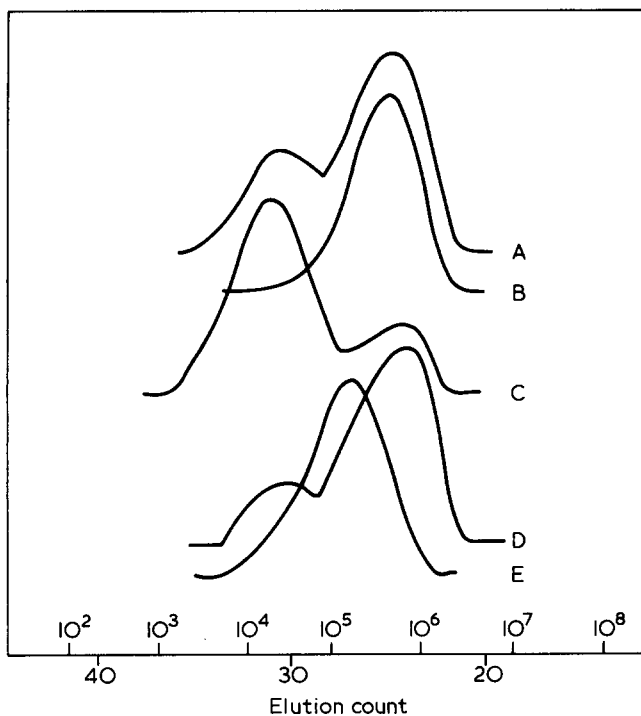**Table 1** Polymerization process and copolymer composition

	Polymn of MAA·Na[a]			Polymn of styrene[b]			
Run no.	(2)/MAA·Na molar ratio	Time (h)	Conversion (%)	Time (h)	Conversion (%)	$[\eta]$[c] (dl g^{-1})	Mole fraction[d] of styrene unit in copolymer
	1.0	144	93.4	–	–	0.93	–
A–1				24	30.2	0.97	0.28
A–2				120	75.9	1.17	0.45

[a] [(2)] = [MAA.Na] = 8.12 × 10^{-2} mol l^{-1}, [KPS] = 8.86 × 10^{-4} mol l^{-1}, in water, temp. 30°C
[b] [Styrene] = 8.12 × 10^{-2} mol l^{-1}, water 5 ml, temp. 30°C
[c] In chloroform at 25°C
[d] Determined by ^1H n.m.r. analysis

Figure 4 G.p.c. curves of (7): curve A, nonfractionated; curve B, fraction (7A); curve C, fraction (7B); curve D, fraction (7C); curve E, poly(methyl methacrylate) (conversion 93.4%)

δ(ppm)
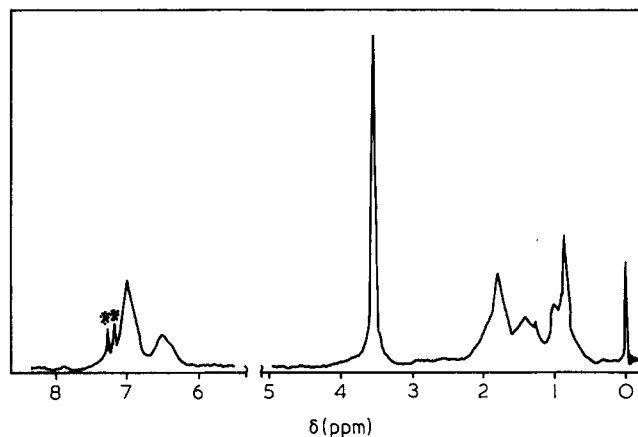
Figure 5 ¹H n.m.r. spectrum of (7C): mole fraction of styrene unit in copolymer, 0.45; solvent, CDCl₃; temperature, 60°C; concentration, 10% w/v; internal standard, TMS. The peaks labelled * refer to protons of chloroform

It has been definitely shown by the results of the above-mentioned block copolymerization of the polymer segment of (2)–MAA·Na with styrene that the AB-type block copolymer can be easily obtained with excellent yield; in other words, active radicals at the growing ends produced in the polymerization of (2)–MAA·Na are maintained in the polymer.

give such a peak at 0.8–0.4 δ as shown in the spectrum of the copolymer obtained by radical copolymerization of methyl methacrylate and styrene[12], but gives a peak at 1.0–0.9 δ. *Figure 5* reveals that there are long chains comprising styrene units[13], which are estimated from the peaks of the methoxy proton and of phenyl proton. The positions of the peaks of the phenyl proton in each styrene unit and of the methoxy proton in each methyl methacrylate unit in the ¹H n.m.r. spectrum of fraction (7B) are similar to those of fraction (7C).

From the results of the fractionation, g.p.c. curves and ¹H n.m.r. spectra, it was found that fraction (7A) mainly consists of polystyrene, while fractions (7B) and (7C) consist of the block copolymer of poly(methacrylic acid-*b*-styrene), though their styrene contents and molecular weights differ from each other. Fraction (7B) is presumed to be block copolymer having comparatively short polystyrene chain.

REFERENCES

1 Robert, A. A., Haszeldine, N. and Smith, S. *J. Chem. Soc. Chem. Commun.* 1976, 260
2 Minoura, Y. and Ogata, Y. *J. Chem. Soc. Jpn., Ind. Chem. Sec.* 1965, **68**, 1748
3 Horie, K. and Mikulasova, D. *Makromol. Chem.* 1974, **175**, 2091
4 Farina, M. and Silvestro, G. D. *J. Chem. Soc. Chem. Commun.* 1976, 842
5 Kabanov, V. A. *J. Polym. Sci. C*, 1975, **50**, 71
6 Lee, M., Morigami, T. and Minoura, Y. *J. Chem. Soc. Faraday Trans. 1* 1978, **14**, 1738
7 Kataoka, S. and Ando, T. *Kobunshi Ronbunshu* 1980, **37**, 375
8 Kataoka, S. and Ando, T. *Polym. Commun.* to be submitted
9 Kataoka, S. and Ando, T. *Kobunshi Ronbunshu* 1980, **37**, 185
10 Kataoda, S. and Ando, T. *Kobunshi Ronbunshu* 1981, **38**, 821
11 Kataoka, S. and Ando, T. *Kobunshi Ronbunshu* 1981, **38**, 797
12 Ito, K. and Yamashita, Y. *J. Polym. Sci. B* 1965, **3**, 637
13 Bovey, F. A., Tiers, G. V. D. and Filipovich, G. *J. Polym. Sci.* 1959, **38**, 73