

Preparation of Soluble Poly(methyl methacrylate-*p*-divinylbenzene) in the Presence of Tetrabromomethane

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ABSTRACT: A method to prepare soluble intramolecularly crosslinked copolymers (microgel) by radical copolymerization of vinyl monomer and divinyl compound was developed. Methyl methacrylate (MMA) and *p*-divinylbenzene (*p*-DVB) was copolymerized in the presence of a high concentration of transfer agent (CBr₄) in benzene. As the ratios of *p*-DVB and CBr₄ to MMA increased, the number average molecular weight decreased and the structure of the microgel became tighter. The soluble polymer was obtained with very high conversion (70—88%). It was confirmed by the characterization of fractionated product that about 50% of the soluble polymers were intramolecularly crosslinked copolymer. The reactivity ratio $r (=k_{13}/k_{12})$ ($M_1 = \text{MMA}$, $M_2 = p\text{-DVB}$, $M_3 = \text{pendant double bond}$) was not constant throughout the course of all the reactions, and became progressively small with time. $r_M (k_{11}/k_{12})$, however, was always constant (0.27). This can be explained if we assume that the intramolecular crosslink is more rapidly formed than that of the intermolecular and a large amount of loops are formed at the early stage of copolymerization.

KEY WORDS Microgel / Transfer Agent / Gel Point / Intermolecular Crosslink / Intramolecular Crosslink / Pendant Double Bond /

Methods for preparing soluble intramolecularly crosslinked copolymers (microgels) by the copolymerization of monomer with divinyl compound have been reported in many papers.¹⁻⁴

In the solution copolymerization of styrene with divinylbenzene containing a transfer agent (diphenyl disulfide), "breaks" are introduced in the propagation and the microgel can be generated with very high conversion and high concentration (74% conversion, 35 g/100 ml polymer concn).³ The character of the soluble products at low conversion has been discussed in detail from the results of their fractionation and characterization of each fraction. It is concluded that as the concentration of the transfer agent is increased, the structure of the microgel becomes more

compact.⁵

In a study on network formation, Rempp pointed out that the decisive factor for intermolecular crosslinking is not consumption of the divinyl compound, but the ability of the pendant double bonds to react with growing radicals and form actual branch points.⁶ To clarify this point, it is necessary to measure the reactivity of the pendant double bond with sufficient accuracy. For this purpose, measurement must be carried out at a high concentration of the chain transfer agent so as to retard the gelation time in reaching a high conversion. These have been the objectives and methods of this study. If the reactive behavior of divinyl compound and pendant double bond is known, we can find the most suitable conditions and routes for preparing soluble

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microgels with the desired structures.

EXPERIMENTAL

Preparation of Microgels

Commercial methyl methacrylate (MMA) and *p*-divinylbenzene (*p*-DVB) were purified by the methods described in a previous paper.⁴ Copolymerization of MMA with *p*-DVB in the presence of transfer agent (tetrabromomethane; CBr₄) were carried out for 50 h in benzene solution with various amounts of *p*-DVB and CBr₄ at 60°C. When infinite networks were formed, they were swollen in benzene for a week to estimate their swelling degree, *Q*. ($Q = (W_b - W_a)/W_a$, where W_a is the weight of dried gel and W_b is that of swollen gel). The soluble products were fractionated and characterized by methods described in previous work.⁴ The molecular weight and intrinsic viscosity were measured to confirm the intramolecular crosslinked structure.

Calculation of r_M and r

When the concentrations of the symmetrical divinyl compound and pendant vinyl group are very small compared to that of monovinyl compound, we need consider only the following equations for the approximate description of the rate of polymerization:

$$\frac{d[M]}{dt} = -k_{11}[M^*][M] \quad (1)$$

$$\frac{d[D]}{dt} = -2k_{12}[M^*][D] \quad (2)$$

$$\frac{d[PV]}{dt} = 2k_{12}[M^*][D] - k_{13}[M^*][PV] \quad (3)$$

where M^* , growing chain radical; M , monovinyl compound; D , symmetrical divinyl compound; PV , pendant double bond; k_{11} , k_{12} , and k_{13} , rate constants.

After dividing eq 1 and 3 by eq 2 and replacing the copolymerization constant $r_M = k_{11}/k_{12}$, $r = k_{13}/k_{12}$, the following set of differential equations were obtained:

$$\frac{d[M]}{d[D]} = \frac{r_M}{2} \frac{[M]}{[D]} \quad (4)$$

$$\frac{d[PV]}{d[D]} = \frac{r}{2} \frac{[PV]}{[D]} - 1 \quad (5)$$

On integrating eq 4 and 5, eq 6 and 7, we obtained:

$$\ln \frac{[D_0]}{[D]} = \frac{2}{r_M} \ln \frac{[M_0]}{[M]} \quad (6)$$

$$[PV] = C \times [D]^{r/2} - \frac{[D]}{1-r/2} \quad (7)$$

where $[D_0]$ and $[M_0]$ are the initial concentrations of D and M , respectively. $C = [D_0]^{1-r/2}/(1-r/2)$.

Copolymerizations were carried out at 60°C under a nitrogen atmosphere. Samples were collected at various reaction times until gelation. The overall conversion was determined by gravimetric measurement, and also calculated from the consumed amounts of M and D determined by high performance liquid chromatography (Japan Spectroscopic Co., Ltd. TRI ROTAR-II). The absorbance of the pendant double bond of each sample, as described in the previous paper,⁵ was measured at 292 nm by Hitachi 124 Spectrophotometer. The absolute quantity of the pendant double bond was determined for several samples by iodine monochloride addition to the vinyl group and successive titration of excess iodine monochloride. From the absorbance and absolute value of PV , the molar extinction function was determined and was used to obtain the content of the vinyl group in other samples. Details of this method have been reported in a previous paper.⁵ From the values of D , M , and PV at various reaction times and from eq 6 and 7, r_M and r were calculated.

RESULTS AND DISCUSSION

Preparation of Microgels

The results of the copolymerization are shown in Table I. It is clearly evident that a

Preparation of Soluble Microgel

Table I. Conditions for preparation and characteristics of the copolymer^a

Sample No.	$[p\text{-DVB}]/[\text{MMA}] \times 10^2$	$[\text{CBr}_4]/[\text{MMA}] \times 10^2$	T_g^b	Yield	Q
			h	%	
1	0.0743	0.096	1.7	90	14.4
2		0.128	1.7	88	12.4
3		0.64	—	85	s
4		1.28	—	88	s
5	0.149	0.128	2.5	61	18.9
6		0.64	22.5	80	c
7		0.96	—	78	s
8		1.28	—	83	s
9	0.743	0.64	7.7	72	9.4
10		1.28	10	66	26.2
11		1.92	—	79	s
12		2.56	—	71	s
13	3.72	3.2	21.7	78	5.9
14		4.3	27.7	74	11.6
15		5.4	—	70	s
16		6.4	—	70	s
17	7.43	1.28	19.7	96	2.1
18		8.0	44	66	12.0
19		9.6	—	72	s
20		11.2	—	71	s

^a $[\text{MMA}] = 4.71 \text{ mol l}^{-1}$, $[\text{AIBN}] = 6.09 \times 10^{-3} \text{ mol l}^{-1}$, 50 h at 60°C in vacuum.

^b Time of gelation.

^c Q could not be measured because of its very large value.

^s Soluble.

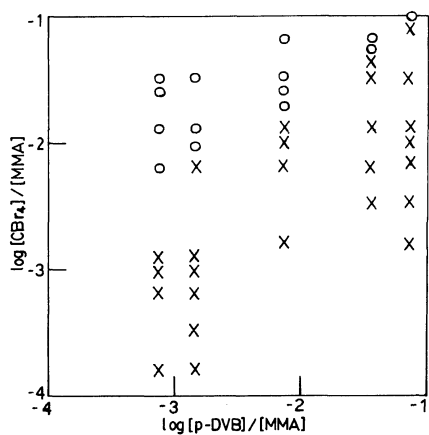


Figure 1. Product profile of the copolymerization of MMA with *p*-DVB in the presence of tetrabromo-methane: ○, soluble; ×, insoluble.

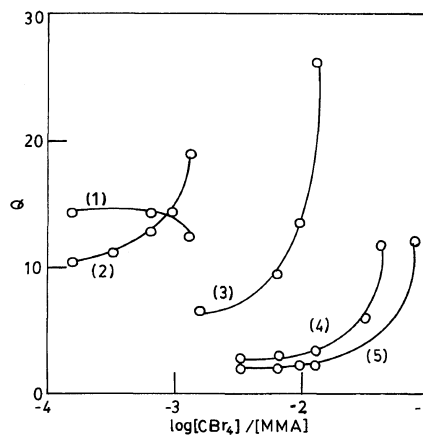


Figure 2. Variation in the equilibrium swelling degree in benzene of MMA-*p*-DVB network as a function of $[\text{CBr}_4]/[\text{MMA}]$: with $[p\text{-DVB}]/[\text{MMA}]$ ratio (1), 7.43×10^{-4} ; (2), 1.49×10^{-3} ; (3), 7.43×10^{-3} ; (4), 3.72×10^{-2} ; (5), 7.43×10^{-2} .

greater amount of CBr_4 is required to prepare soluble product as p -DVB increases, and the conversion of the soluble copolymer exceeds 70%.

The ranges of microgel or macrogel formation are shown in Figure 1 as a function of the molar ratios of p -DVB/MMA and CBr_4 /MMA. A wide range of soluble microgels were formed. The same observations can be made from the equilibrium swelling degree (Q) of insoluble products (Figure 2). Q increased rapidly as the concentration of CBr_4 increased progressively to the boundary where soluble and insoluble polymers were formed. This increase in Q could not be observed at p -DVB/MMA ratio 7.43×10^{-4} . In this case, the primary polymer with high degree of polymerization was formed because of the low concentration of CBr_4 . p -DVB content was so small that almost all of p -DVB and the pendant vinyl group were consumed at the first stage of reaction, considering the reactivity. The macrogel may have formed at the first stage of the reaction and the product contained a large amount of the linear polymer.

Characters of Fractionated Microgels

Several characteristics of the fractionated polymers (Sample No. 8 and 16) are shown in Table II. The molecular weight of 16 series polymers is clearly smaller than that of 8 series polymers. The yield of the linear polymer in the former was about 50%, and about 60% in the latter. Considering that $[\text{CBr}_4]_{(8\text{-series})}/[\text{CBr}_4]_{(16\text{-series})}$ was 5 and the ratio of the p -DVB concentration in two series of copolymerization was 25, it is clear that the addition of chain transfer agent is very effective for decreasing molecular weight.

Influence of AIBN and CBr_4 on Yield

In Tables III and IV, with increasing initiator or chain transfer agent, the yield of the product at the gel point increases. In the case of sample No. 25, no macrogelation could be observed for an extended reaction time (18 h)

Table II. Characteristics of fractionated sample No. 8 and 16 polymers

Fraction No.	wt %	$[\eta]^a$ ml g ⁻¹	$M_n^b \times 10^{-4}$	$[\eta]/[\eta]^c$
8-f1	8	54.6	89.2	0.281
f2	19	38.0	27.6	0.556
f3	9	29.6	16.7	0.677
f4	6	26.8	14.3	0.703
f5	11	22.6	9.3	*
f6	29	18.2	5.9	*
f7	18	13.7	3.2	*
16-f1	13	15.8	20.2	0.306
f2	8	12.7	12.1	0.387
f3	12	10.6	6.4	0.573
f4	15	10.2	3.8	0.864
f5	10	8.7	2.2	*
f6	10	8.3	1.7	*
f7	31	7.3	1.5	*

^a The intrinsic viscosity of the copolymer at 40°C in THF.

^b The number average molecular weight calculated from the universal calibration of GPC.

^c $[\eta]$, the intrinsic viscosity of linear poly(MMA) having the same M_n as the copolymer.

* About 1.

Table III. Reaction conditions and characteristics of the copolymers^a

Sample No.	$[\text{CBr}_4]/[\text{MMA}] \times 10^2$	$[\text{AIBN}]$ mol l ⁻¹	T_g h	Yield %
21	0.80	0.0052	18	36.6
22	0.80	0.0206	7	47.2
23	0.80	0.0822	4.3	68.6
24	1.60	0.0206	11	64.1
25	3.20	0.0206	18 ^b	83.3

^a Polymerization conditions: $[\text{MMA}] = 1.89 \text{ mol l}^{-1}$ [p -DVB] = $6.94 \times 10^{-2} \text{ mol l}^{-1}$ at 60°C, in N_2 .

^b Gelation time was not observed at 18 h.

and at high conversion (83.3%). It seems that not only crosslinking by the propagation reaction but also termination occurred mainly intramolecularly since the increase in AIBN promoted microgel formation.

In Table IV, the pendant vinyl group decreases more rapidly with increasing concen-

Preparation of Soluble Microgel

Table IV. Characteristics of the copolymers

No.	Reaction time	Yield	<i>p</i> -DVB Conversion	[<i>p</i> -DVB] ^a × 10 ²	[PV] ^b
	h	%	%	mol l ⁻¹	mol l ⁻¹
21-1	3	0.68	25.2	5.19	—
-2	5	2.83	39.0	4.23	0.948
-3	7	5.82	48.1	3.60	1.65
-4	9	9.65	65.1	2.42	2.19
-5	12	16.9	77.3	1.58	3.09
-6	15	27.1	88.6	0.791	3.86
22-1	2	2.8	49.5	3.50	0.473
-2	3.5	10.7	75.9	1.67	1.14
-3	4.5	20.2	88.5	0.798	1.37
-4	5.5	30.3	95.3	0.326	1.06
-5	6.0	35.6	97.2	0.194	1.20
-6	6.5	40.8	98.1	0.132	1.40
23-1	2.0	16.5	87.5	0.868	1.25
-2	2.3	25.1	93.4	0.458	1.58
-3	2.7	35.6	96.6	0.236	1.88
-4	3.0	40.6	98.6	0.0972	1.65
-5	3.3	47.4	99.2	0.0552	1.54
-6	3.7	55.7	99.7	0.0208	1.19

^a [*p*-DVB] remains in the reaction solution.

^b Concentration of pendant double bond in the reaction solution.

tration of AIBN at the same concentration of CBr₄. This is difficult to explain. It seems that the affinity of the isobutyronitrile radical to MMA or the pendant vinyl group causes this phenomenon. There are no data to support this supposition, but a radical similar to the isobutyronitrile radical certainly shows this tendency: M₁ methacrylonitrile, M₂ styrene; $r_1 = 0.16$. M₁ methacrylonitrile, M₂ MMA; $r_1 = 0.65$.⁸ A similar result was obtained for acrylonitrile–styrene and for acrylonitrile–MMA systems.⁸

Determination of r_M and r

Different values of r_M have been reported in the literature.^{4,7} The slope of the line obtained by a plot of the data in Table V, gave 0.27 as r_M . This value agrees well with our previous result (0.28).⁴ The double bond in *p*-DVB is more reactive and, therefore, more rapidly consumed than MMA.

Table V. Values of r calculated from each stage of copolymerization

Expt. No.	r
21-1	—
2	9.54
3	4.34
4	2.60
5	1.28
6	0.666
22-1	16.7
2	4.40
3	2.44
4	1.92
5	1.43
6	1.13
23-1	2.76
2	1.66
3	1.10
4	0.908
5	0.816
6	0.762

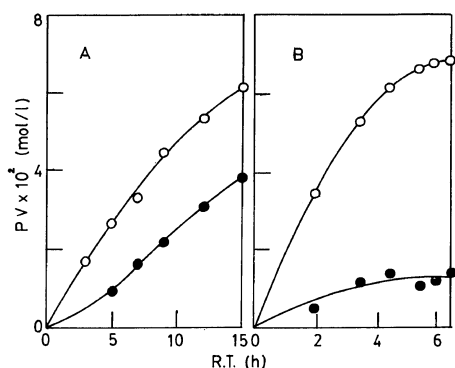


Figure 3. Formation and residue of the pendant double bonds vs. reaction time: (A, sample No. 21; B, sample No. 22); ○, formation; ●, residue of pendant double bonds.

The values of r (k_{13}/k_{12}) in Table V become progressively smaller as the reaction proceeds. Possible explanations for this are as follows: The supposition that k_{12} (reaction between MMA radical and DVB) changes with conversion seems unrealistic. The change in r must arise from variation in k_{13} calculated by eq 7 derived from eq 2 and 3. Equation 3 is an approximate expression of the consumption of PV, and k_{23} (reaction between DVB radical and PV) and k_{33} (reaction between PV radical and PV) must be considered for accurate expression. From the same reason in the case of k_{12} , it is difficult to realize the change in k_{23} . A rational expression is possible when k_{33} changes as the reaction proceeds. As reported by Soper, Haward and White,⁷ and Shindo, Sugimura, Horie, and Mita,⁹ the main crosslinking occurs when reactions of this type are intramolecular. In this study, this was found to be the case. In Table V and Figure 3, at low

conversion of MMA (below 10%) even though a sufficient excess of PV to form microgel was consumed, the gel point was greatly retarded. Considering these results, k_{33} corresponds to intramolecular crosslinking by PV groups if it occurs. Condensation of vinyl groups on a polymer chain takes place at the first stage of copolymerization. Consumption of this group by the reaction corresponding to k_{33} proceeds rapidly so that k_{13} evaluated by eq 7 was overestimated.

Although there remain some uncertainties regarding r , it was confirmed that, by increasing both the transfer agent and divinyl compound, polymer chains formed at the first stage of polymerization are more extensively crosslinked intramolecularly, and consequently, a relatively large number of small rings are formed.

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