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Vinyl Polymerization. 411. Experimental Supports for the Concept of Hard and Soft Hydrophobic Areas and Monomers in the So-called Uncatalyzed Polymerization

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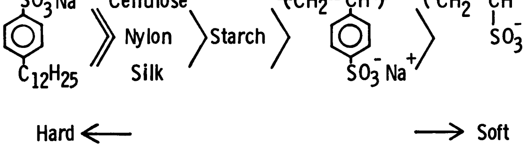
We have proposed a concept of hard and soft hydrophobic areas (HA) and monomers. In order to verify such a concept, two series of experiments were carried out. Poly(styrene-alt-disodium maleate) (**1**) and poly(styrene-alt-sodium methyl maleate) (**2**) were used as initiating macromolecules for the copolymerizations of styrene/methyl methacrylate (MMA) and acrylonitrile/MMA. When **1** was used, MMA was more easily polymerized than styrene. Inversely, when **2** was used, styrene was more easily polymerized than MMA. Poly(styrene-co-sodium acrylate) (**3**) substances with various compositions were used as intiators for the copolymerizations. The produced copolymers of MMA and styrene were found to have a larger content of MMA as the mole ratio of acrylate in **3** became higher. Inversely, the produced copolymers of MMA and acrylonitrile had a larger content of acrylonitrile as the mole ratio of acrylate became higher. Those results could be reasonably explained by the concept of hard and soft hydrophobic areas and monomers.

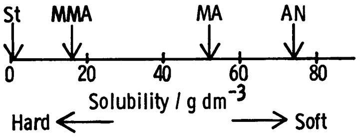
Macromolecules having a hydrophilic group, such as starch, cellulose, polyamide and enzyme, can initiate the radical polymerization of vinyl monomers in water without any ordinary radical initiator. Such a simple and novel polymerization has been called an "uncatalyzed polymerization."[1–3] It has been clarified that the polymerization proceeds as follows: (i) the macromolecules form the hydophobic areas (HA) in a water phase, (ii) the vinyl monomer dissolves in the water phase and then is incorporated into HA, and (iii) in the HA, a radical polymerization proceeds.

Needless to say, the hydrophobicities of HA and monomers differ from each other. We called the more HA and hydrophobic monomers "hard," and the less HA and hydrophilic monomers "soft." The orders of hardness and softness of HA and monomers are expressed by Fig. 1.[2,4]

We have proposed "a concept of hard and soft HA and monomer," which means that the hard HA prefers to incorporate the hard monomer, while the soft HA prefers to incorporate the soft monomers.[2] This concept has been verified experimentally in several papers[2,4] by two methods, *i.e.*, by the coplymerization of styrene with methyl methacrylate (MMA) and by the selectivity of the monomer initiated with copolymers having different hydrophobicities.[5]



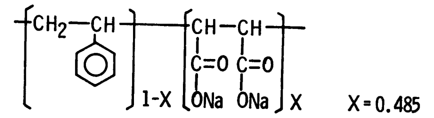
(a) Hard and soft HA



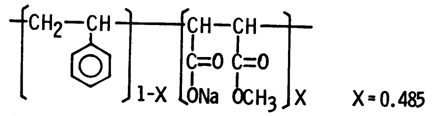
(b) Hard and soft vinyl monomers$^{a)}$

Fig. 1. Hard and soft HA and monomers.
St: Styrene, MMA: methyl methacrylate, MA: methyl acrylate, AN: acrylonitrile. a) The numbers indicate the solubilities into water at 20 °C.

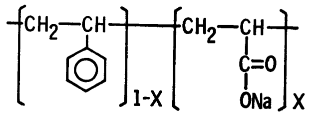
The present paper deals with the polymerizations of styrene, MMA, and acrylonitrile initiated by the water-soluble poly(styrene-alt-disodium maleate) (Copolymer **1**) or poly(styrene-alt-sodium methyl maleate) (Copolymer **2**), and with the copolymerizations of styrene with MMA and of MMA with acrylonitrile initiated with poly(styrene-co-sodium acrylate) (Copolymer **3**) substances with different compositions.



Copolymer 1, poly(styrene-alt-disodium maleate)



Copolymer 2, poly(styrene-alt-sodium methyl maleate)



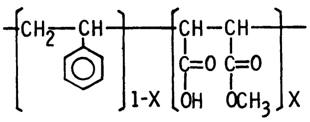
Copolymer 3, poly(styrene-co-sodium acrylate)

Experimental

Materials. The monomers were purified by the usual methods and distilled under a vacuum before use. Ion-exchanged and distilled water was used as the solvent.

Preparation of Poly(styrene-alt-disodium maleate) (Copolymer 1). Five cm^3 (43.3 mmol) of styrene and 4.25 g (43.3 mmol) of maleic anhydride (Manh) were dissolved in 5 cm^3 of benzene and then placed in a tube. The tube was sealed after thawing with nitrogen and heated at 60 °C for 100 h. After the reaction, the contents were poured into large amounts of hexane to precipitate the copolymer. The copolymer was twice reprecipitated from acetone and benzene/hexane (1 : 2 by vol.). The yield was 99%. The mole fraction of Manh in the copolymer was determined by elemental analysis to be 0.485. Accordingly, the copolymer was mostly alternative. The molecular weight of the obtained poly(styrene-alt-Manh) was measured by the vapor-pressure osmometric method and found to be 1.79×10^4 in acetone at 37 °C. This copolymer was neutralized with calculated amount of a 1 mol dm^{-3} NaOH solution up to pH 10 and then freeze-dried.

Preparation of Poly(styrene-alt-sodium methyl maleate) (Copolymer 2). The poly(styrene-alt-Manh) described above was refluxed in dried methanol for 50 h and then poured into large amounts of water to precipitate the copolymer. By elemental analysis, the copolymer was found to be a monoester with the structure shown below. This acidic copolymer was changed into its sodium salt by neutralization with a 1 mol dm^{-3} NaOH solution at pH 10 and then freeze-dried.



X=0.485

Poly(styrene-co-sodium acrylate) (Copolymer 3). Four kinds of Copolymer **3** (x=0.291, 0.537, 0.698, 0.782) and poly (sodium acrylate) (x=1.00) were prepared and purified by the method reported in a previous paper.[5] Here, x means the mole fraction of the sodium acrylate unit in Copolymer **3**.

Copolymers **1**, **2** and **3** were confirmed by the KI or ESR method to contain no peroxide moiety nor free radical.

Procedures of Polymerization. The vinyl monomers, Copolymer **1**, **2**, or **3** and water were placed in a tube. The tube was sealed under a vacuum after thawing with nitrogen and then incubated at 85 °C with or without shaking. After a certain time, the contents of the tube were poured into a large amount of methanol in order to precipitate the polymer produced. The conversion of the monomer was calculated from the weight of the polymer.

Results and Discussion

Polymerization of Vinyl Monomers Initiated by the Copolymer 1 or 2. An aqueous solution of Copolymer **1** or **2** was shaken with styrene, MMA, or acrylonitrile at 85 °C for 3 h. The results obtained are listed in Table 1.

The HA formed by Copolymer **1** is softer than the HA formed by Copolymer **2**; the hardness of the monomer is in order of: styrene>MMA>acrylonitrile. Accordingly, styrene was more easily incorporated in the HA formed by Copolymer **2** than in that formed by Copolymer **1** and more easily polymerized by Copolymer **2** than by Copolymer **1**, but MMA was, inversely, more easily polymerized by Copolymer **1** than by Copolymer **2**. Acrylonitrile is too soft to be easily incorporated into either Copolymer **1** or **2**.

TABLE 1. POLYMERIZATION OF VINYL MONOMERS WITH THE COPOLYMER **1** OR **2**[a)]

Copolymer	Conversion[b)]/%		
	Styrene	MMA	Acrylonitrile
1	3.30	5.59	0.14
2	5.44	5.04	0

a) Monomer, 3 cm^3; copolymer, 0.03 g; H_2O 10 cm; 85 °C; 3 h; with shaking. b) Each conversion contains the thermal conversion.

Copolymerization of MMA with Styrene or Acrylonitrile by Copolymer 3. The copolymerizations of MMA with styrene or acrylonitrile initiated by Copolymer **3** with various compositions were carried out.

The HA formed by Copolymer **3** having a higher x fraction are softer than those formed by Copolymer **3** having a lower x fraction.

First, a mixture of styrene and MMA and an aqueous solution of Copolymer **3** was allowed to stand at 85 °C for 3 h. The copolymers produced from the upper monomer layer and the lower aqueous layer were

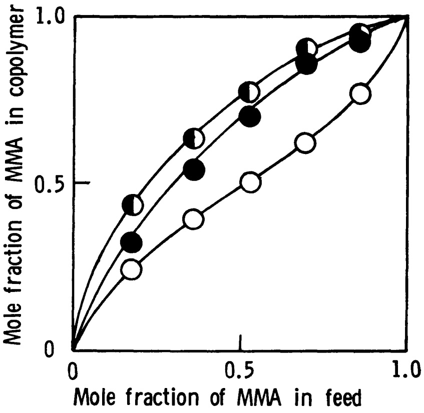


Fig. 2. Composition curves in the copolymerization of styrene and MMA on standing.
(MMA+styrene) 3 cm^3; Copolymer **3**, 0.03 g; H_2O 10 cm^3; 85 °C; 3 h.
—○—: Composition curve of the copolymers produced in monomer layer (x of Copolymer **3**=0.537), —●—: composition curve of the copolymers produced in water layer (x of Copolymer **3**=0.537), —◐—: composition curve of the copolymers produced in water layer (x of Copolymer **3**=0.782).

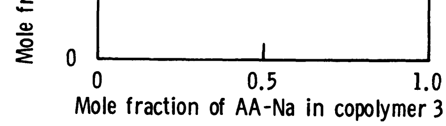


Fig. 3. Effects of the mole fraction of AA–Na in Copolymer **3** on the composition of copolymer produced in the water layer. Copolymer **3**, 0.03 g; H_2O, 10 cm^3; 85 °C; 8 h; on standing.
●: MMA, 1.5 cm^3; styrene, 1.5 cm^3 (mole ratio of MMA: styrene =0.48 : 0.52). ●: MMA, 1.5 cm^3; acrylonitrile, 1.5 cm^3 (mole ratio of acrylonitrile: MMA =0.38 : 0.62).

isolated separately. The conversions of the monomer mixture in the water phase were controlled as to be lower than 2.2%. The composition curves are shown in Fig. 2.

The curve of open circles indicates the composition curve of the copolymer produced in the monomer layer. Here, a usual thermal polymerization proceeds. Accordingly, the curve was very similar to that of an ordinary radical-copolymerization curve.

The black and half-black circles in Fig. 2 indicate the results obtained by Copolymer **3** having x values of 0.53 and 0.78 respectively. The latter copolymer forms a softer HA than the former copolymer. Accordingly, the copolymer of 0.78 of x is considered to incorporate MMA more easily than styrene. As is to be expected by the concept, the contents of MMA in the copolymer of MMA with styrene produced by Copolymer **3** of $x=0.78$ are larger than in those produced by Copolymer **3** of $x=0.53$.

A second support was given by the copolymerizations of MMA/styrene and MMA/acrylonitrile on standing, using Copolymers **3** with various compositions. The results obtained are shown in Fig. 3. In both copolymerizations, the mole ratios of the monomers in the feed were kept constant, while the composition of Copolymer **3** was varied. The abscissa of the figure indicates the x-value of Copolymer **3**. In the copolymerization of MMA and styrene, the curve shown by black circles was obtained. Clearly, the contents of MMA in the copolymer produced increased with the increase in the x-value.

Inversely, in the copolymerization of MMA and acrylonitrile, the contents of MMA in the copolymer produced decreased with the x-value.

These results can be explained by the difference in the incorporated amounts of the monomer into the HA formed by Copolymer **3** with various compositions. That is, they show the propriety of the concept of hard and soft HA and monomer.

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