Application of Macromonomers for Pressure Sensitive Adhesives II. Phase Separation and Adhesive Properties

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Pressure sensitive adhesives (PSA) were prepared by copolymerization of butyl acrylate, methyl methacrylate and styrene macromer and the effects of macromer on the adhesive properties and phase separated structures were investigated. The results are as follows:

(1) The cohesion of the PSA increased as the quantity of the styrene macromer increased.
(2) The reason why the cohesion of the PSA increased seemed to be that the polystyrene phase, as the graft chain, was separated from the polybutyl acrylate phase as matrix.
(3) When styrene was used instead of styrene macromer, there were not these effects on the adhesive properties.

KEY WORDS Poly(styrene methyl methacrylate/butyl acrylate) copolymers; random copolymers; adhesive properties; surface-chemical properties; molecular structure; phase separation.

1 INTRODUCTION

As one can see from the patents[1,2] already granted for tests of the application of graft copolymers as pressure sensitive adhesives, those investigations can be said to have reached the stage of practical use. Yet it seems that there remains a certain inadequacy in their scientific treatment.

However, for some time now all sorts of methods have been used to form graft copolymers, and as long ago as in 1972 an epoch-making procedure was proposed by Milkovich *et al.*[3,4] in the U.S.A. That is known as the macromer (macromonomer) technique. The macromer technique is being studied in various fields at present for its potential to provide precisely defined graft copolymer structures.

Attempts to bring these characteristics of the macromer into existence in pressure sensitive adhesives have already been made and published in patents.[5,6] It is a matter of course that pressure sensitive adhesives are basically composed of soft compo-

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nents and hard components, their performance being determined by the balance of that combination. It may also be said that when graft copolymers are being applied as pressure sensitive adhesives their adhesive properties are governed by their composition and, of course, by their structures. This means that clarification of the relationship between the structures and adhesive properties of graft copolymers is a matter of great interest.

We have already used pressure sensitive adhesives made from styrene macromers and butyl acrylate macromers and reported on the relationship between their adhesive properties and surface chemical characteristics.[7]

In this study, we have synthesized a P(BA-co-MMA-g-S) graft copolymer by macromerization with an eye to the microphase-separated structure characteristic of the graft copolymer and discussed the effect of styrene macromer on adhesive properties, particularly on cohesive strength, and changes in the structure of pressure sensitive adhesives brought about by the introduction of macromer.

2 EXPERIMENTAL METHODS

2.1 Specimens

Styrene macromer (McS) used was ARCO Chemical Co.'s Chemlink 4500 (2-styrylethyl methacrylate, molecular weight 13,000). Commercial reagents were distilled and used for butyl acrylate (BA), styrene (S) and methyl methacrylate (MMA). Special grade commercial reagents were used in their normal condition for ethyl acetate, methanol and toluene. Commercial special grade reagent was used refined by recrystallization for azo-bis-isobutyronitrile (AIBN). For the elution solvent in gel permeation chromatography (GPC), we used commercial first grade tetrahydrofuran filtered with a Teflon membrane filter of $3\mu m$ pore diameter.

2.2 Polymerization

All polymerization was by radical solution polymerization. As a polymerization vessel we used a test tube of 24mm diameter sealed under reduced pressure after nitrogen substitution. The polymer obtained was precipitated with methanol and refined by re-precipitation with ethyl-methanol acetate.

2.3 Determination of Molecular Weight Distribution

Molecular weight distribution of the polymer obtained was measured by a GPC (Model 6000A) manufactured by Waters Co. The polymer refined in 2.2 was dissolved in THF to give a 0.8g/dl solution and was filtered with a membrane filter of pore diameter $0.5\mu m$ and used as a specimen. Measurement was conducted using THF as the elution solvent at a column temperature of 35°C, and a flow velocity 1 ml/min. A refractometer was used as the detector. Eight kinds of monodisperse polystyrene in a molecular weight range of 1,800 to 2,700,000 were used as standard samples.

2.4   Calculation of McS Polymerization Yield

McS polymerization yield was obtained by determining the peak area of unreacted McS in the GPC chromatogram. We first made a number of kinds of McS solution of known concentration, took GPC chromatograms with various changes in infusion volume and made calibration curves of McS infusion volume and peak area. Having obtained by wave form analysis program the peak area of unreacted McS among the sample polymers, the McS polymerization yield was obtained from the previous calibration curve. For systems not containing McS, the polymerization yields were obtained by the usual polymerization method.

2.5   Measurement of Glass Transition Temperature (Tg)

The Tg of polymer refined in 2.2 was determined by using a differential scanning calorimeter of Daini Seikoosha Co. manufacture.

2.6   Application of Pressure-Sensitive Adhesives

Polymer refined in 2.2 was dissolved in ethyl acetate to give a 40 wt% concentration, applied to polyethylene terephthalate (PET) film of average thickness of 25μm to give a dry coating weight of $30g/m^2$ and dried in an electric furnace at 100°C for 3 min. The adhesive tape obtained was aged for a day at room temperature and used as a test sample.

2.7   Measurement of 180° Peel Strength

Adhesive tape from 2.6, above, was cut into small card shapes 1 inch in width and stuck onto a stainless steel plate (SUS304). After it had been applied, the adhesive tape was pressed on with a 400g rubber roller passed over it back and forth 10 times. The steel plate used was degreased beforehand with toluene. 180° peel strength was measured with an Autograph (SD-100 type) of Shimazu Seisakusho Co. manufacture at a pull velocity of 200mm/min.

2.8   Ball Tack Measurement

Ball tack was measured by the J. Dow method. Steel balls (dia $1/32''$ to $32/32''$) were allowed to roll on a 10cm runway, a plane of 30° inclination, the diameter of the largest of the balls that stopped completely for 5 s on the 10cm length of adhesive tape being taken as the tack.

2.9   Holding Power Measurement

Adhesive tape was stuck onto a steel plate (SUS304) to provide a contact surface of 25mm × 25mm and was pressed onto it by passing a 400g rubber roller over it back and forth 10 times. Holding power was assessed by the time it took until a 1 kg weight hung on this test sheet fell at 40°C. Unless specifically stated otherwise, adhesive properties are based upon JIS Z0237.

2.10   Contact Angle Measurement

The adhesive tape prepared in 2.5 was made into samples for measuring contact angles by sticking it onto a glass slide using double sided tapes, with its adhesive surface upward. The apparatus used to measure contact angles was based on the improved pattern drop shape method and measured the contact angles of the water and methylene iodide on the adhesive surface of the glass plate. For details of the apparatus and the method of obtaining contact angles, please see our earlier paper (Part I).

2.11   Calculation of Surface Free Energy

The surface free energy of the adhesives, γ_s (dispersion force component, γ_s^d; polar force component, γ_s^p) was calculated by equation (1) and equation (2) combining the Owens method[9] which extends the Fowkes method[8] and the Young method.[10]

$$(1 + \cos\theta) \cdot \gamma_L/2 = (\gamma_s^d \cdot \gamma_L^d)^{1/2}$$

$$+ (\gamma_s^p \cdot \gamma_L^p)^{1/2} \tag{1}$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{2}$$

Here γ_L is the surface tension of the contact medium, while γ_L^d and γ_L^p are, respectively, its dispersion force component and polar force component.

2.12   Transmission Electron Microscope (TEM) Observation

A 0.8wt% ethyl acetate solution of the polymer refined as in 2.2 was deposited by capillary tube drop by drop onto a mesh with carbon support membrane already attached and after thorough drying, ruthenium tetroxide staining was conducted at an environmental temperature of 30°C. It was confirmed beforehand that the homopolymers are not stained and that the PS phase only is stained.

3   RESULTS AND DISCUSSION

3.1   Polymerization

In Table I, instead of sample polymers and McS produced by the macromer method, there are shown the composition and physical properties of sample polymers produced with S monomer. Polymerization was conducted at 70°C and feed concentrations and monomer concentrations were regulated so that the divergence in molecular weights between samples might be as small as possible. The result was that when McS was used the molecular weights obtained were from 350,000 to 510,000, and when S monomer was used the molecular weights were from 270,000 to 330,000. Furthermore, all glass transitions were at about −50°C. The polymeriza-

TABLE I
Preparation[1] and properties of sample polymers

Sample no.	Monomer in feed (wt%)			Conc.[3] of AIBN (wt%)	Polymn. time (hr.)	$\overline{M}_W$ ($\times 10^{-5}$)	$\overline{M}_W/\overline{M}_N$	T_g (°C)
	BA	MMA	McS[2]					
1	80	20	—	0.4	7	3.5	1.9	−51
2	80	15	5	0.4	7	3.9	2.3	−50
3	80	10	10	0.4	4	5.1	2.2	−50
4	80	5	15	0.6	6	4.9	2.5	−51
5	80	—	20	1	27	4.4	2.8	−50

[1]Copolymerization in ethyl acetate by AIBN at 70°C: total monomer: 50wt% (No. 5; 40wt%).
[2]Polystyrene macromer.
[3]Concentration to total monomer.

Sample no.	Monomer in feed (wt%)			Concn. of monomer (wt%)	Polymn. time (hr.)	$\overline{M}_W$ ($\times 10^5$)	$\overline{M}_W/\overline{M}_N$	T_g (°C)
	BA	MMA	S					
H-1	80	20	—	50	7	2.7	3.0	−50
H-2	80	15	5	50	22	3.3	2.4	−50
H-3	80	10	10	60	24	3.3	2.3	−50
H-4	80	5	15	60	50	3.1	2.4	−50
H-5	80	—	20	60	50	2.8	2.1	−51

[1]Copolymerization in ethyl acetate by AIBN at 70°C: concn. of AIBN, 0.1wt% to monomer (No. H-1; 0.4wt%).

tion yield of samples using S monomer obtained by polymerization were for H-1 100%, H-2 95%, H-3 87%, H-4 83% and thereafter, with H-5 at 70%, declined as the S content increased.

3.2 Molecular Weight Distribution

Figure 1 shows the GPC curves of the polymers obtained. On the left side of the diagram there are those with McS, while on the right side are those with S monomer. As the diagram shows, in the polymers with McS, peaks of unreacted McS are to be seen at the positions of elution volume 55ml and molecular weight 13,000. When the areas of these peaks were obtained by wave form analysis and polymerization yields of McS from the area-infusion volume calibration curves obtained from the McS single GPC chromatograms of previously known volume were calculated, all the values were high, with No. 2 at 91% and No. 3 to 5 each at 94%. Furthermore, they were used in this state in the tests below without any special removal of unreacted McS. Other polymers which used S monomer all showed single peaks. We next evaluated the adhesive properties of these polymers.

3.3 Evaluation of Adhesive Properties

Adhesive properties when McS was used are shown in Figure 2 for the weight proportion of McS/MMA at the time of preparation. Here, those polymers whose McS/MMA proportion is 0/100 were taken to have assumed the form of P(BA-co-
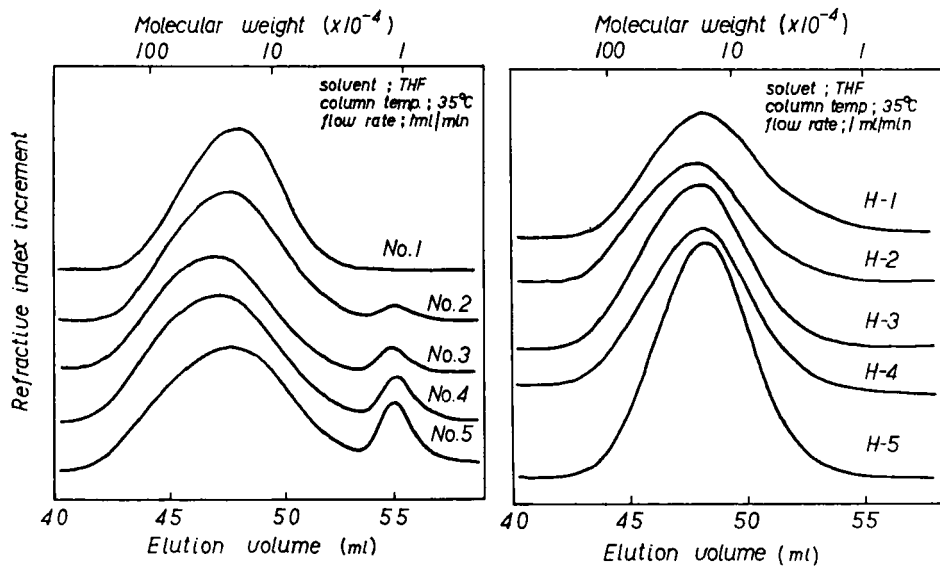
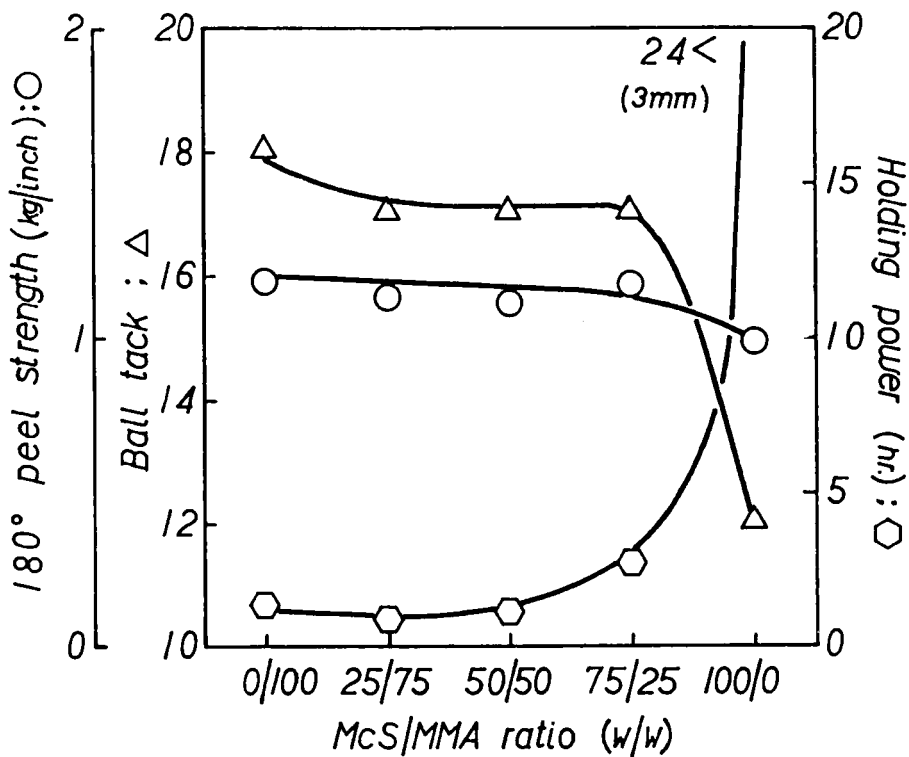FIGURE 1   GPC chromatograms of sample polymers.

FIGURE 2   Adhesive properties of sample polymers prepared by macromer technique. Conditions of measurement: 180° peel strength, 24°C, 200 mm/min; J. Dow ball tack, 21°C; holding power, 40°C.

MMA) random copolymers and those whose McS/MMA is 100/0 to have assumed the form of P(BA-g-S) graft copolymers. The composition proportions used below are all those at the time of preparation. It is clear from the diagram that 180° peel strengths were roughly uniform (about 1kgf/inch) regardless of McS/MMA and were all interfacial failures at that. Against this, ball tack at 17 to 18 was more or less constant with McS/MMA ratios at from 0/100 to 75/25 but declined abruptly to 12 when the McS/MMA ratio became 100/0. Then, in contrast with this, holding power showed a roughly constant value with McS/MMA ratios of from 0/100 to 50/50, but with McS/MMA ratios of 75/25 to 100/0 it increased dramatically, and when the McS/MMA ratio reached 100/0 it showed the highly superior result of more than 24 h. This increase in holding power is thought to be attributable to the fact that S introduced as a graft chain had become a structure capable of more effectively exhibiting the cohesive strength of an adhesive, that is to say a microphase-separated structure collectively forming a domain. We now compare the changes in adhesive properties when S is used instead of McS. In Figure 3 the adhesive properties of each sample are shown against the S/MMA weight ratio at preparation. It is clear from the diagram that there is the same kind of tendency as when McS was used. The failure conditions in the 180° peel strength were all interfacial failures. However, whenever there was a decline in ball tack in instances of large weight percentages of S it was greater than when McS was used, and at the S/MMA ratio of 100/0 it fell to as low as 8. Again, the rate of increase in holding power also became smaller than when McS was used, and even with the S/MMA ratio at 100/0 it was as low as
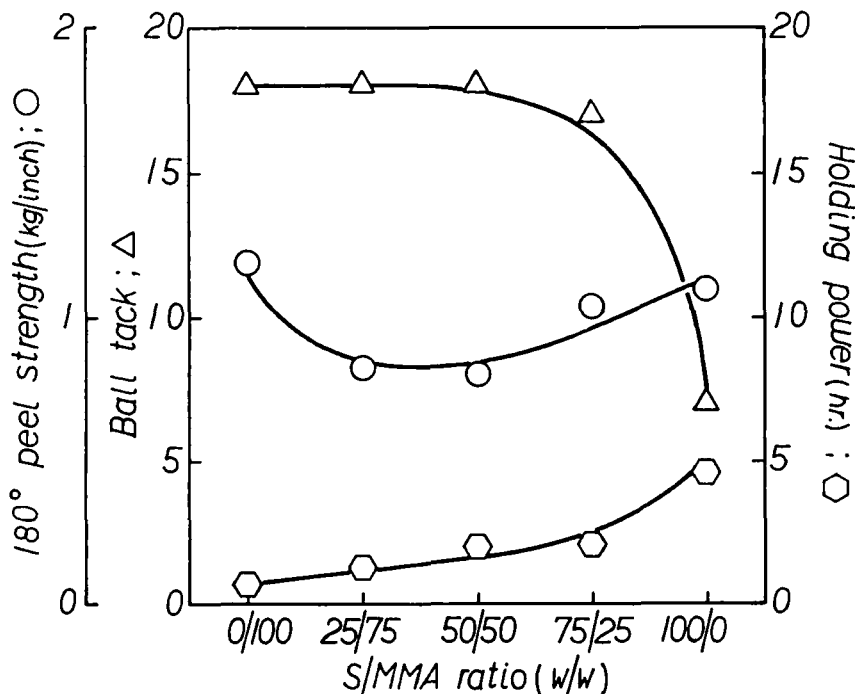

FIGURE 3   Adhesive properties of sample polymers. Conditions of measurement: 180° peel strength, 25°C, 200 mm/min; J. Dow ball tack, 24°C: holding power, 40°C.

5 h at the most. When the above results are put together it can be considered that when the S component is introduced into the adhesive P(BA-co-MMA) copolymer its introduction as a graft chain is more effective in improving the cohesive power of an adhesive than a simple random copolymerization. Regarding the decline in ball tack it is considered that owing to the fact that the cohesive strength of the adhesive had been increased, the fluidity of the adhesive surface had declined and tack had been lowered because the wetting power of the adhesives had decreased, but this point will be dealt with in the future.

We next examined the surface characteristics of the pressure-sensitive adhesives in order to gain some insight into the formation of the phase structure.

3.4 Surface Characteristics of Pressure-Sensitive Adhesives

In Figures 4 and 5 there is shown the surface free energy, γ_s, of pressure-sensitive adhesive surfaces when McS was used and when S was used instead of McS. Also shown in these diagrams are the dispersion component γ_s^d and the polar component γ_s^p. Surface free energy was obtained by measuring the contact angles of water and ethylene iodide on the film cast from the ethyl acetate solution of each sample polymer and calculating according to the equation shown in Figure 4. It is clear from Figure 4 that γ_s remained roughly constant regardless of the McS/MMA feed
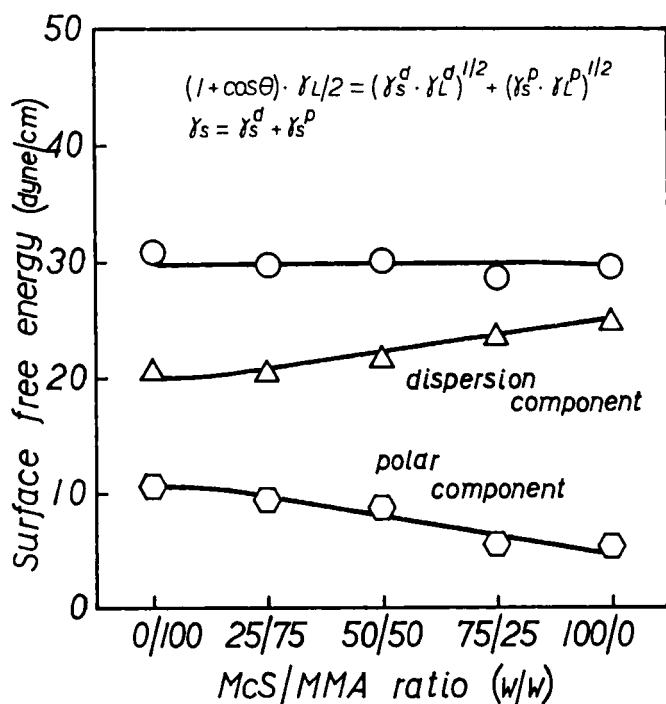

FIGURE 4   Surface free energy of sample polymers prepared by macromer technique.
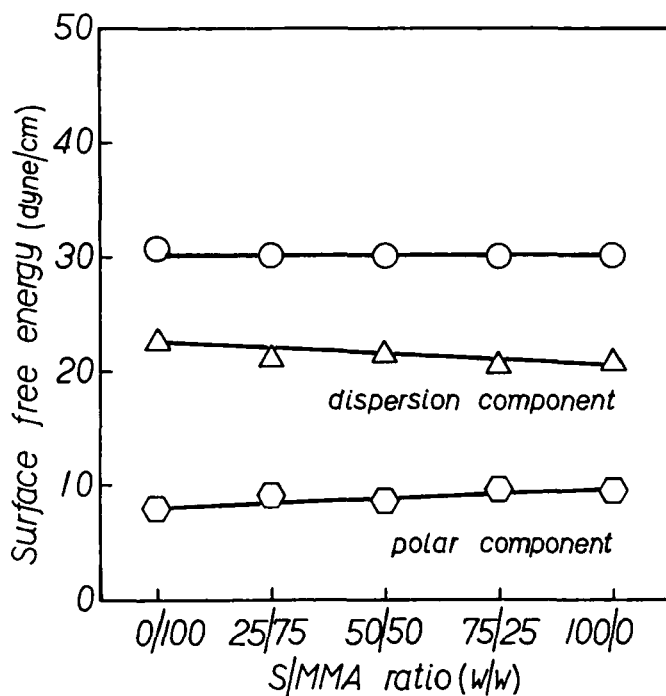
FIGURE 5   Surface free energy of sample polymers.

ratio. However, γ_s^d increased together with increase in the weight percentage of McS, while on the other hand γ_s^p declined. This means that there has been a change in the hydrophobic property of the film surface demonstrating that the concentration of the graft chain PS segments has increased on the surface. That is to say, it is believed that in samples No. 3, 4, and 5, those with particularly large McS content among the samples prepared by the macromer technique, PS segments had certainly been introduced as graft chains with the result that surface activity appeared, the pressure sensitive adhesive surface changing to hydrophobic. Consequently, the possibility was suggested that a predicted phase-separated structure in which graft copolymers, in general, would occupy the bulk of the pressure sensitive adhesive had, in fact, been formed by the PS phase and the PBA phase. On the other hand, when S was used instead of McS, no change was to be seen either in γ_s^d or γ_s^p, as is clear from Figure 5, and no phase structure is to be expected. The fact that there is no change in γ_s in any instance in Figures 4 and 5 can be explained by the absence of appreciable change in the critical surface tension of PS from that of PBA or PMMA. Therefore, it is thought that the fact that there was no change in adhesive power even with change in the McS/MMA ratio or the S/MMA ratio was because there was no change in surface free energy.

Next, the presence of the phase structure was confirmed by TEM observation.
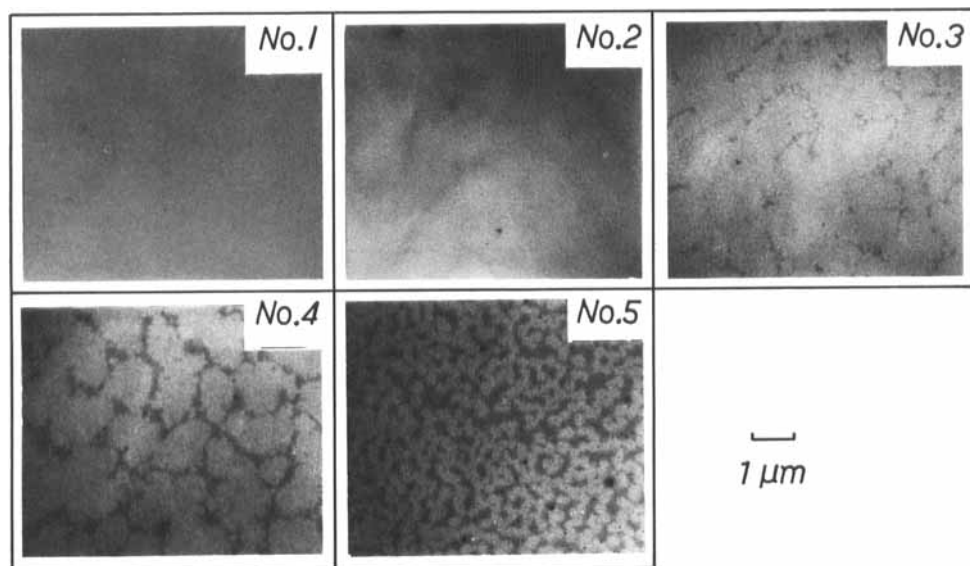
FIGURE 6   Transmission electron micrographs of sample polymer films cast from ethyl acetate; stained by RuO_4 at 25°C.
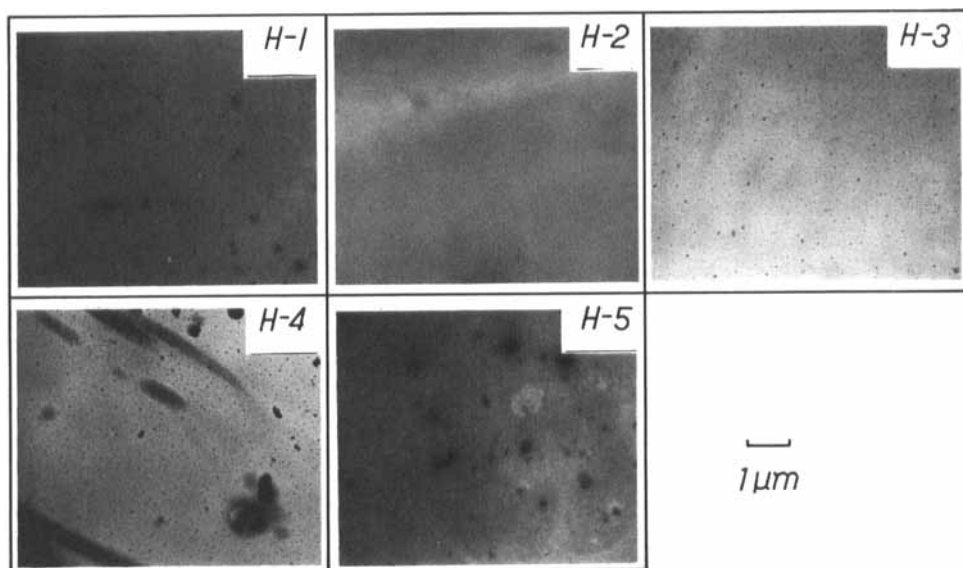

FIGURE 7   Transmission electron micrographs of sample polymer films cast from ethyl acetate; stained by RuO_4 at 25°C.

3.5 TEM Observation

TEM micrographs are shown in Figures 6 and 7. It was confirmed by staining homo-polymers of BA and MMA, which were separately synthesized, that ruthenium tetroxide, the stain used in this test, stains only PS. Consequently, the sections of the micrographs that look dark are the PS phase, while the light sections are PBA and PMMA phases. As is clearly shown in Figure 6, a phase-separation structure, not to be seen in No. 1 and No. 2, can be seen in Nos. 3 to 5, the proportion occupied by the dark-stained PS phase growing in size with increase in the McS weight percentage. This is thought to show that the the PS segments introduced as graft chains had come together and phase-separated from the matrix of the PBA phase. In Figure 7 it was not possible to confirm the presence of this kind of phase-separated structure in samples prepared from S instead of McS.

CONCLUSION

The cohesive power of pressure sensitive adhesives was conspicuously increased by replacing part of the MMA in pressure sensitive adhesives consisting of BA and MMA with styrene macromer. This is believed to have resulted from the PS compo-nent's introduction by the macromer technique as pressure sensitive adhesive polymer graft chains and the resultant microphase-separation performed by the PS phase and the PBA phase. However, no such effect was obtained when styrene was used instead of polystyrene macromer.

Acknowledgment

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