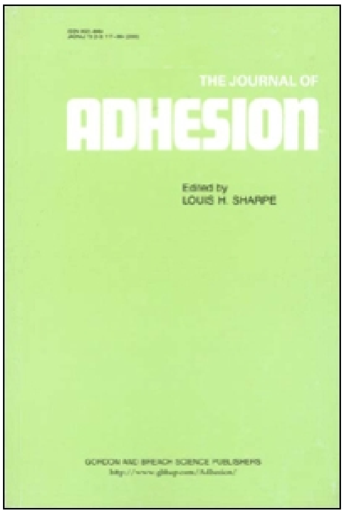

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Application of Macromonomers for Pressure Sensitive Adhesives I. Adhesive and Surface Properties

Katsuhiko Nakamae[a]; Tatsuo Sato[a]; Tsunetaka Matsumoto[a]
[a] Faculty of Engineering, Kobe University, Nada-ku, Kobe, Japan

To cite this Article Nakamae, Katsuhiko , Sato, Tatsuo and Matsumoto, Tsunetaka(1991) 'Application of Macromonomers for Pressure Sensitive Adhesives I. Adhesive and Surface Properties', The Journal of Adhesion, 36: 2, 85 — 96
To link to this Article: DOI: 10.1080/00218469108027064
URL: http://dx.doi.org/10.1080/00218469108027064

J. Adhesion, 1991, Vol. 36, pp. 85–96
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United Kingdom

Application of Macromonomers for Pressure Sensitive Adhesives
I. Adhesive and Surface Properties*

KATSUHIKO NAKAMAE, TATSUO SATO and TSUNETAKA MATSUMOTO

Faculty of Engineering, Kobe University, Rokkoudai-cho, Nada-ku, Kobe 657, Japan

Adhesive and surface-chemical properties of poly(styrene macromer-butyl acrylate) copolymers, poly (styrene-butyl acrylate macromer) copolymers and poly (styrene-butyl acrylate) random copolymers were investigated. The results were as follows:

(1) The adhesive properties of the copolymers which were prepared by the macromer-technique were different from the random copolymers.
(2) It was found that there were differences in the surface and molecular structure between the copolymers which were prepared by the macromer technique and the random copolymers. These differences were evident from the results of measurements of the surface free energy of the copolymers and of the interfacial tension of water/toluene in the presence of the copolymers.
(3) The reason why there were differences in the surface and molecular structure seemed to be that the copolymers which were prepared by the macromer technique had graft chains and a different inner-structure from the random copolymers. Therefore, it was suggested that the graft copolymers which were prepared by the macromer technique had a phase-separated structure.

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

1 INTRODUCTION

Because graft copolymers, like block copolymers, chemically combine two polymers with different properties to form microphase-separated structures, they can display higher functionality than conventional random copolymers; moreover, as this is a matter of surface activity, they are characterized by the fact that it is possible to reform at will the surfaces of the high-molecular materials which constitute their basic substances.

Incidentally, there have been all kinds of methods used in the past to synthesize graft copolymers, but in 1972 an epoch-making procedure was suggested by Milkovich *et al.*[1,2] in the U.S.A. That was what is called the macromer (macromonomer) technique. Because macromerization is capable of providing graft copoly-

---

*Translated from the Japanese and published with the kind permission of The Adhesion Society of Japan. Originally published in *Nihon Setchaku Kyokaishi* [J. Adhesion Soc. Japan] **26**(3), 100–105 (1990).

mers of precisely defined structure, its application is being tested at present in rubber, adhesives and paints as well as in the surface reforming of textiles, plastics, films, etc. and even in such areas as anti-clotting materials and permselective membranes in the field of medical materials.

Because, as previously stated, graft copolymers are composed of two high molecules of different character, they can be adapted to pressure sensitive adhesives. Investigations have already been conducted in this area also, and offered in the form of two or three patents.[3,4] Needless to say, pressure sensitive adhesives are basically composed of a soft component and a hard component, their performance being determined by the balance of the combination. And when graft copolymers are applied to pressure sensitive adhesives as well, it may safely be said that their stickiness is governed by the composition and, even more, by the structure, of the graft copolymers. That is to say, it is a matter of very great interest to clarify the relationship between the structure of the graft copolymer, or the chemical character of the adhesive surface, and stickiness.

With this investigation we have introduced the comparatively new procedure of macromerization to pressure sensitive adhesives and have gone into the relationship between the chemical character of the pressure sensitive adhesive surface and its stickiness.

2 EXPERIMENTAL METHOD

2.1 Samples

The styrene macromer (McS) used was Arco Chemical's Chemline 4500 (2-polystyrylethyl methacrylate), (molecular weight 13,000); the butyl acrylate macromer (McBA) was that offered by Nihon Carbide Kogyo (molecular weight 2,100). Butyl acrylate (BA) and styrene (S) were commercial reagents used after distillation. Ethyl acetate, tetrahydrofuran (THF) and toluene were commercial special grade used as received. Azo-bis-isobutyronitrile (AIBN) was commercial special grade and was used after refining by recrystallization. As the elution solvent in gel permeation chromatography (GPC) we used commercial first grade THF filtered with a Teflon membrane of 3μm pore diameter.

2.2 Polymerization

All polymerization was carried out by radical solution polymerization. For polymerization we used 25mm diameter test tubes sealed under reduced pressure after nitrogen displacement.

2.3 Measurement of Molecular Weight Distribution

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

2.4 Measurement of Limiting Viscosity Number ([η])

The [η] of polymers obtained was measured according to the usual method with an Uberode type capillary viscometer. The measurement was conducted at 30°C with THF as solvent.

2.5 Measurement of the Viscosity

The various shear stresses and shear rates of the solutions of the polymers obtained were measured by E-type viscometer (EMD-Type) of Tokyo Keiki manufacture. Shear rates and shear stresses were calculated by the following equations:

$$Ds = 2\pi\ N/60\ \phi \tag{1}$$

here, Ds : shear rate
N : rotor revs.
ϕ : rotor conical angle (rad)

$$S = 3T\ \alpha/200\pi\ R^3 \tag{2}$$

here, S : shear stress (dyn/cm^2)
R: rotor radius (cm)
α : indicator scale read value
T : gauge full scale torque (dyn/cm)

In the E-type viscometer used in this experiment $\phi = 0.027$ rad, R = 2.4cm and T = 14.374 dyn/cm.

Viscosity was calculated from the following equation.

$$Q = S/Ds \times 100 \tag{3}$$

here Q: viscosity (cps)

2.6 Coating of Pressure Sensitive Adhesives

Solutions of the polymers obtained were coated onto polyethylene terephthalate (PET) film of 25μm average thickness to give a dry coating weight of 30g/m^2 and dried 3 min in an electric furnace at 100°C. The adhesive tape thus obtained was aged at room temperature for a day and used as test samples.

2.7 Measurement of 180° Peel Strength

The adhesive tape was cut into 1″ small card shapes and stuck onto stainless steel plates (SUS 304). After being applied it was pressed on by a 400g rubber roller passed over it 10 times back and forth. The steel plate was used after degreasing beforehand with toluene. 180° peel strength was measured with an Autograph (SD-100 Type) of Shimazu Seisakusho manufacture at a pull rate of 200mm/min.

2.8 Ball Tack Measurement

Steel balls (diameters 1/32″ to 32/32″) were allowed to roll on a 10cm-long inclined plane runway (angle of inclination 30°), the diameter of the largest steel ball to have stopped completely for 5 s on the 10cm-long adhesive tape being taken as the tack.

2.9 Measurement of Holding Power

Adhesive tape was stuck onto a stainless steel plate (SUS 304) to give an adhesive surface of 25mm × 25mm and was then pressed on by a 400g rubber roller passed over it back and forth 10 times. Holding power was appraised after hanging a 1kg weight on this test piece by the time it took that weight to fall at 40°C. Unless otherwise specified, the above-mentioned appraisal of stickiness was in accordance with JIS Z0237.

2.10 Measurement of Contact Angles

Adhesive tape prepared in 2.6 was stuck onto glass slides, using double sided tape, with its pressure sensitive adhesive surface upward and used as samples for the measurement of contact angles. With contact angle measuring apparatus based on the improved drop shape method we measured the contact angles of water and methylene iodide on the pressure sensitive adhesive surface on the glass plate. This measuring apparatus is one capable of scanning the drops of liquid formed on the pressure sensitive adhesive with a video monitor, so we calculated the contact angle when the drop was being enlarged (advancing contact angle; θ_a) and then when it was being diminished (retreating contact angle; θ_r) from equation (4) and equation (5) using the height of the liquid drop and the diameter of the contact surface of the read off by the video monitor. Measurement was made 15 times for each specimen. Maximum and minimum values were discarded and the remaining 13 values were averaged arithmetically.

When θ_a (or θ_r) $\leq 90°$

$$\theta_a\,(\text{or } \theta_r) = 2\tan^{-1}(2H/R) \tag{4}$$

When θ_a (or θ_r) $>90°$

$$\theta_a\,(\text{or } \theta_r) = 90 + \cos^{-1} \cdot ([R \cdot H/|H^2 + (R/2)^2|]) \tag{5}$$

Here H and R are, respectively, the height of the liquid drop and the diameter of the contact area of the sample. The contact angle θ was then obtained by equation (6).

$$\theta = \cos^{-1}[(\cos\theta_a + \cos\theta_r)/2] \tag{6}$$

2.11 Calculation of Surface Free Energy

The surface free energy, γ_s (dispersion component, γ_s^d; polar component, γ_s^p) of the pressure sensitive adhesives was calculated by equation (7) and equation (8) combining the Owens method[6] expanding the Fowkes method,[5] and the Young equation.[7]

$$(1+\cos\theta)\cdot\gamma_L/2=(\gamma_s^d\cdot\gamma_L^d)^{1/2}+(\gamma_s^p\cdot\gamma_L^p)^{1/2} \tag{7}$$

$$\gamma_s=\gamma_s^d+\gamma_s^p \tag{8}$$

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

2.12 Interfacial Tension Measurement

Each copolymer was dissolved in toluene to provide a 10^{-3}, 10^{-2} and 10^{-1}g/dl concentration and then the interfacial tension of these toluene solutions of the copolymers with water was measured at 25°C with a du Nouy-type interfacial tensiometer of Shimazu Seisakusho manufacture. The toluene solutions of each polymer were gently poured into measuring dishes in which water had been placed and after standing for 2 h the interfacial tension was measured.

3 RESULTS AND DISCUSSION

3.1 Polymerization

Shown in Table I are the polymerization conditions and the characterization of the sample polymers used. Samples No. 1 to 3 were prepared with St macromer, No. 7 to 9 with BA macromer, while No. 4 to 6 are ordinary random copolymers. The molecular weights of the copolymers with St macromer were as high as around

TABLE I
Preparation[a] and characterization of P(St-BA) copolymers

Sample no.	St in feed wt%	Mn × 10^4 GPC	Mw/Mn GPC	Mp[b] × 10^4 GPC	$[\eta]$[c]
1	10	10.3	3.3	27.0	0.672
2	20	9.4	3.6	24.0	0.657
3	30	8.8	4.0	24.0	0.627
4	10	2.2	2.0	5.4	0.235
5	20	1.1	2.6	3.8	0.190
6	30	1.1	2.2	2.8	0.168
7	10	1.7	3.1	2.5	0.102
8	20	1.7	3.5	2.5	0.118
9	30	1.6	4.6	2.5	0.137

[a] Copolymerization at 70°C in ethyl acetate by AIBN: total monomer; 40wt%, AIBN; 1.5wt% to total monomer.

[b] Molecular weight at peak of GPC chromatogram.

[c] Measured in THF at 30°C.

Sample No. 1–3; P(St macromer-BA) graft copolymers,
Sample No. 4–6; P(St-BA) random copolymers,
Sample No. 7–9; P(St-BA macromer) graft copolymers.

100,000 while the molecular weight of copolymer with monomer and with BA macromer (samples nos. 4–9) were as low as around 20,000 or 30,000.

What is more, limiting viscosity numbers were in good agreement with the tendency of the molecular weights. In Figure 1 the GPC chromatograms of Nos. 1, 4 and 7 are shown as an example. No. 5 and 6 were the same shape as No. 4, and No. 8 and 9 were the same shape as No. 7. Here the small peaks to be seen in No. 1 and No. 7 each correspond to the position of the molecular weight of the macromer and can be regarded as unreacted macromer. In this instance the macromer was used as received, without specially refining it or removing the unreacted macromer.

3.2 Appraisal of Viscosity

Figure 2 shows the viscosity of polymer solutions measured by the E type viscometer. Styrene volumes at the time of preparation are shown on the horizontal axis. It is clear from the diagram that preparations with St macromer and random copolymers showed a decline in viscosity with increase in St content but, in contrast with

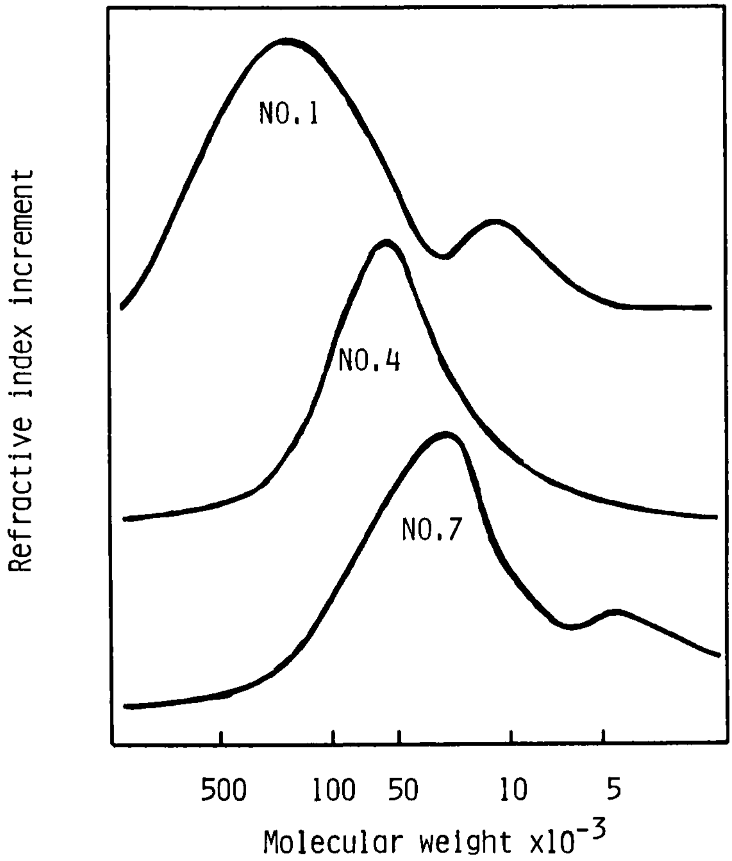

FIGURE 1 GPC chromatograms for P(St-BA) graft and random copolymers.

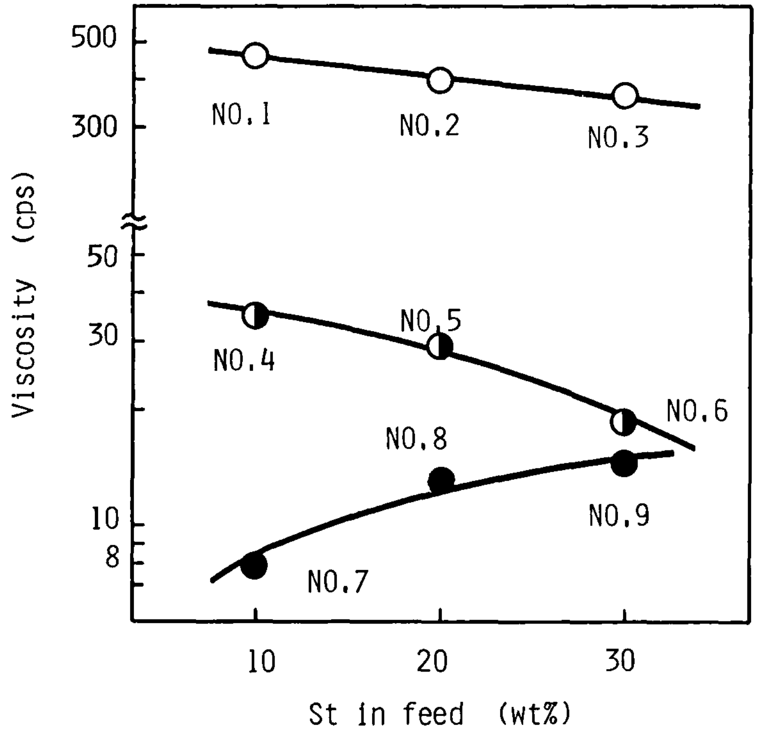

FIGURE 2 Viscosity of P(St-BA) graft and random copolymer solutions. Rate of shear, 38.4 sec^{-1}; Temperature, 30°C.

this, the viscosity showed a rise when BA macromer was used. These tendencies are in good agreement with the results for molecular weights and limiting viscosity numbers.

3.3 Evaluation of Adhesive Properties

In Figure 3 is shown 180° peel strength when SUS 304 was used as the adherend. Styrene concentration in the feed is shown on the horizontal axis. When St macromer was used, the peel strength declined with increase in the St content but the failures were all interfacial with the adherend. As against this, with preparations using BA macromer and with random copolymers, the failure occurring in all cases was cohesive failure, and the peel strength grew with increase in St concentration. But in the case of No. 9, the piece of adhesive tape was seen to have crinkled and peeled away from the adherend, so that it can be regarded as an instance of lowered apparent strength due to increase of the cohesive strength of the adhesive, making for an interfacial failure with PET. Therefore, it can be imagined that St monomer in copolymer with BA macromer is effective in increasing the cohesive strength of the adhesives prepared with St-BA random copolymer, leading to interfacial failure with sample No. 9.

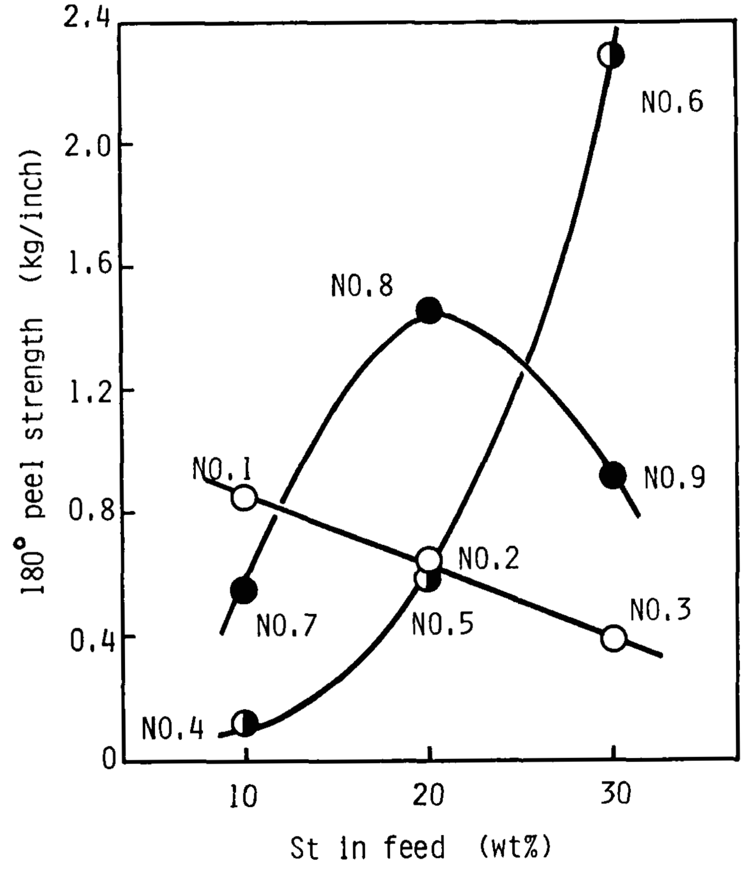

FIGURE 3 180° peel strength of P(St-BA) graft and random copolymers.

Figure 4 shows the results of ball tack tests. The tack of preparations using St macromer and random copolymers declined with increase in the St concentration in the feed. However, tack could not be measured in any composition using BA macromer.

Figure 5 shows as holding power the time until a 1kg weight fell at 40°C. Styrene concentration in the feed is shown on the horizontal axis. In all instances the holding power increased with increase in St concentration, its effectiveness being greatest when used with St macromer, next with BA macromer, then with random copolymers. Furthermore, although it cannot be said that feed composition on its own entirely reflects the composition of the copolymers, if one looks carefully at the fact that the smallest unit of all the macromers used in this experiment is methacrylate and its copolymeric nature can be regarded as being about the same as low molecular weight methacrylate monomer, then it can be inferred that the composition of the copolymer and the composition of the feed are roughly alike. So, viewed as the same feed composition, holding power was highest when St macromer was used and

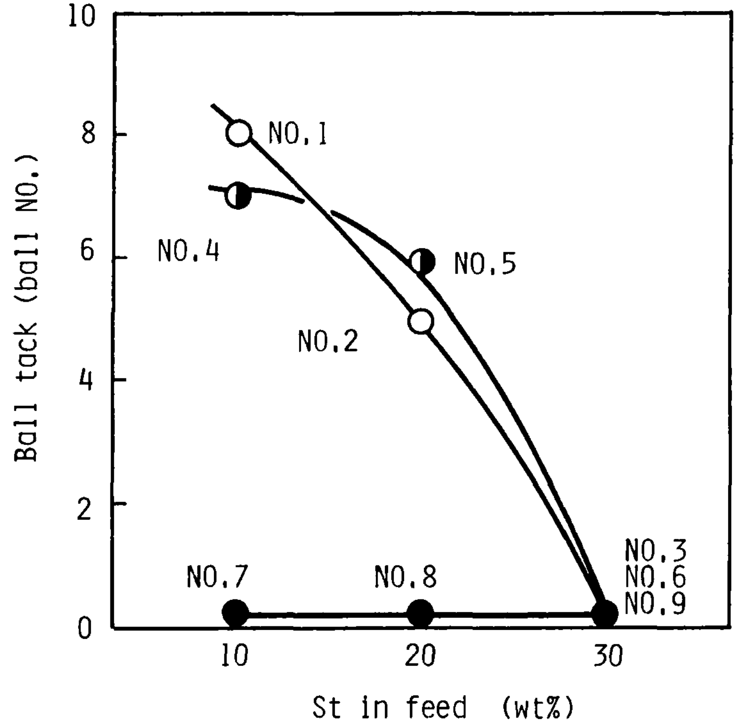

FIGURE 4 Ball tack of P(St-BA) graft and random copolymers.

next to that when BA macromer was used, while random copolymer showed the lowest value.

When the above results of viscosity were brought together with the properties of pressure sensitive adhesives, the effect St macromer had in increasing cohesive strength was particularly great. Moreover, also when BA macromer was used there was a noticeable improvement in cohesive strength thought to be an effect of PSt segments in changing cohesive failure into interfacial failure which accompanied increase in St concentration. On the other hand, random copolymer adhesives were themselves soft and their cohesive strength was the lowest.

Next we examined the surface structure of these copolymers.

3.4 Surface Chemical Properties

In Figure 6 there are shown the surface free energies of the copolymers calculated by geometric averaging from the contact angles of water and methylene iodide on the pressure sensitive adhesive surfaces. As Figure 6 shows, in each of the series with conceivably different internal structures, there appear different values for surface free energy. This demonstrates that within each series there are significant differences in the surface structures. In like manner, it was demonstrated from the fact that copolymers with St macromer or BA macromer have surface structures

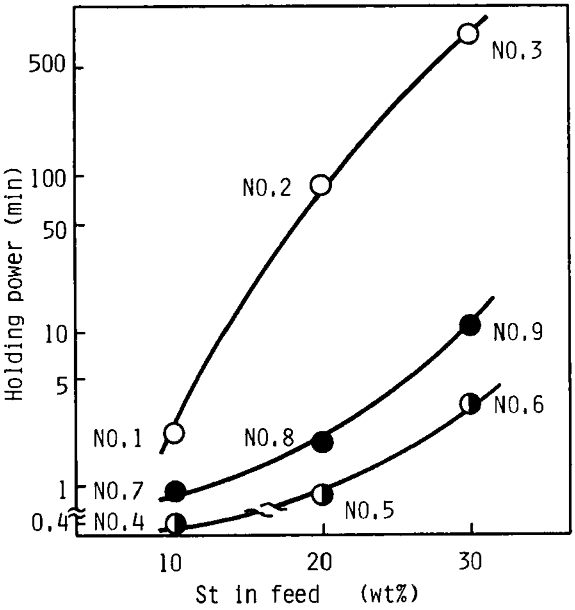

FIGURE 5 Holding power of P(St-BA) graft and random copolymers.

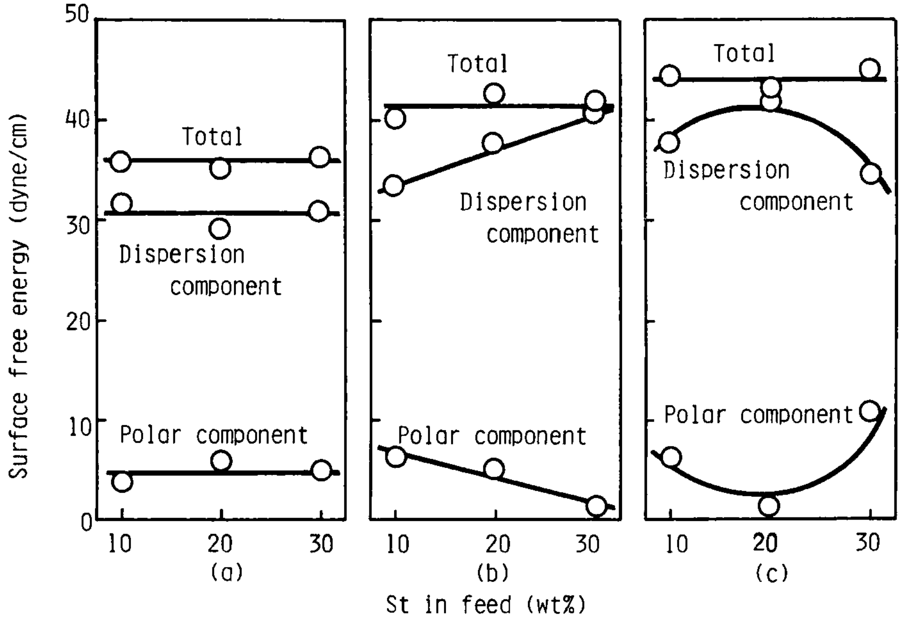

FIGURE 6 Surface free energy of P(St-BA) graft and random copolymers, (a); P(St macromer-BA) graft copolymers, (b); P(St-BA) random copolymers, (c); P(St-BA macromer) graft copolymers.

that are different from those of random copolymers and, moreover, display separate adhesive behaviour, that copolymers with macromers have different molecular structures from those of random copolymers.

Next, in order to gain further insight into those molecular structures, we measured the interfacial tension between dilute toluene solutions of each copolymer and water.

3.5 Interfacial Tension

Figure 7 shows interfacial tension of water/toluene on the vertical axis and copolymer concentrations on the horizontal axis. From the fact that the surface tension is greater with BA macromers than with random copolymers, as the diagram shows, it can be thought that the polymer molecules assume a more readily assembled form at the water/toluene interface. In other words, to judge from the fact that compared with random copolymers the copolymers prepared by macromer-technique possess the quality of readier orientability at the interface, or so-called surface activity, graft copolymers are obtainable with macromer-copolymerized systems as expected. It is also considered that the reason for the greater effectiveness when BA macromer is used than with St macromer is that PBA segments with higher polarity than St are functioning effectively.

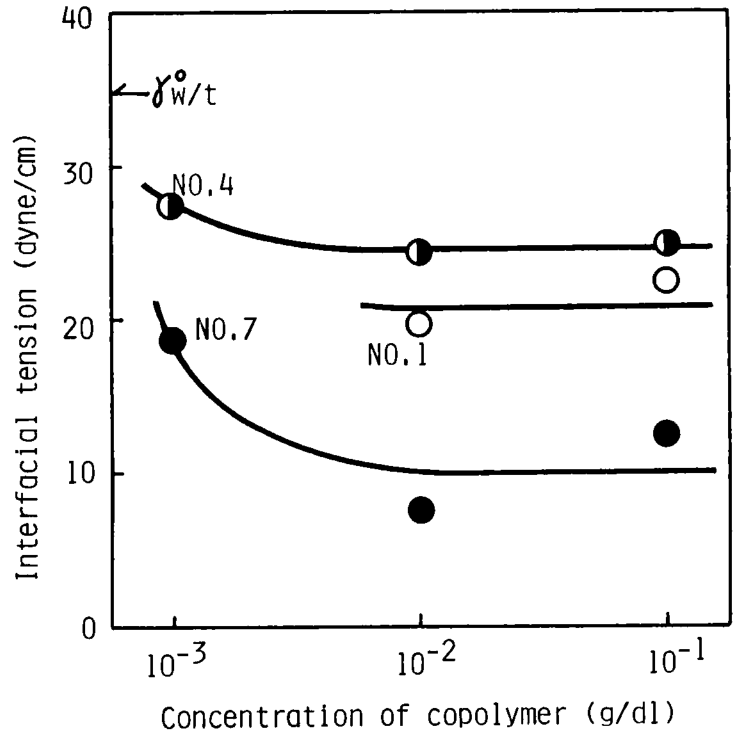

FIGURE 7 Relationship between the interfacial tension at the water-toluene interface and concentration of P(St-BA) copolymers, $\gamma^{o}_{w/t}$ is the interfacial tension at the water-toluene interface.

4 CONCLUSION

Adhesive and surface chemical properties or the relationships between structural differences of graft copolymers prepared with St macromer and BA macromer and having, respectively, PSt and PBA segments and for random copolymers consisting of St and BA were investigated.The results were that different adhesive properties were shown owing to the differences in structure of the copolymers; in particular, those with PSt introduced widely improved the cohesive strength of the pressure sensitive adhesive. Again, the fact that differences had developed in those surface structures, as well, was inferred from the results of the surface free energy measurements of pressure sensitive adhesives. From the results of surface tension with a dilute system, it was considered that those pressure sensitive adhesives with macromer had different surface free energy and, also from these results, it was considered that those with macromer had molecular structure different from random copolymers, that is to say, that a graft structure had been formed. Further, from the above facts it was demonstrated that there probably exists some kind of phase structure in graft copolymers prepared by the macromer technique.

Acknowledgment

This research has received assistance from Shorai Science and Technology Promotion Foundation for which we offer our warmest thanks. It also was presented in part at the 24th Symposium on Adhesion and Adhesives (1986, Osaka).

References

1. R. Milkovich, M. T. Chiang, U. S. Patent, 3786116; 3842059; 3862101; 3918255.
2. R. Milkovich, "Anionic Polymerization Kinetics, Mechanism and Synthesis," J. E. McGrath, Ed. *ACS Symp. Ser.* **166,** 41 (1981).
3. Patent Shoo 56-59882. (In Japanese)
4. Patent Shoo 59-75975. (In Japanese)
5. F. M. Fowkes, *J. Phys. Chem.*, **66,** 328 (1962); *ibid.* **67,** 2538 (1963).
6. D. K. Owens, R. C. Wendt, *J. Appl. Polym. Sci.*, **13,** 1741 (1969).
7. D. H. Kaelble, *Physical Chemistry of Adhesion* (John Wiley and Sons, New York, 1971), pp. 149–183.