

# Effects of the Chemical Structure on the Heat Resistance of Thermoplastic Expandable Microspheres

Yasuhiro Kawaguchi,<sup>1</sup> Yosuke Itamura,<sup>2</sup> Kenjiro Onimura,<sup>2</sup> Tsutomu Oishi<sup>2</sup>

<sup>1</sup>Tokuyama Sekisui Company, Limited, 4560 Kaisei-Cho, Syuunan, Yamaguchi, 746-0006 Japan

<sup>2</sup>Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube, Yamaguchi, 755-8611 Japan

Received 1 June 2004; accepted 11 October 2004

DOI 10.1002/app.21429

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The effects of various additional non-nitrile-containing monomers on the heat resistance of thermoplastic expandable microspheres containing acrylonitrile and methacrylonitrile were investigated to determine the correlation between the chemical structure and expandable properties. Thermoplastic expandable microspheres were synthesized by suspension polymerization, with acrylonitrile and methacrylonitrile as the main ingredients and seven kinds of methacrylic acid derivatives, methacrylic acid, and acrylic acid as non-nitrile-containing monomers. The expandable properties, that is, the maximum expansion temperature, the expansion start temperature, and the maximum dimension change, were measured with thermomechanical analysis.

For the development of heat-resistant microspheres, polymer structures with smaller functional free volumes, higher glass-transition temperatures, and higher cohesive energy densities, such as methyl acrylic acid, were applied as non-nitrile-containing monomers. Molecular structures such as —COOH groups with strong electrostatic interactions and hydrogen-bonding forces were found to be suitable for high heat resistance. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1306–1312, 2005

**Key words:** blowing agents; copolymerization; radical polymerization

## INTRODUCTION

Thermoplastic expandable microspheres consist of a drop of liquid hydrocarbon, encapsulated by a gas-proof and polymeric shell. The liquid hydrocarbon, used as the blowing agent, is contained in a 3–7- $\mu\text{m}$ -thick shell.

When expandable microspheres are heated to 80–190°C, the microspheres expand, reaching a volume 50–100 times bigger than before. The different thermomechanical behaviors of the various grades make it possible to select an optimal grade for each process and application. This phenomenon is used in printing inks to obtain three-dimensional patterns on paper, wallpaper, textiles, and so forth.<sup>1–5</sup>

The microspheres are prepared by a suspension-type polymerization of droplets of a mixture of a monomer and a blowing agent. Their manufacturing method was first described in a Dow Chemical Co. patent,<sup>6</sup> and since then there have been many other patents.<sup>7–10</sup>

Japanese patent 5-15499 (1993) describes a method of producing thermoplastic expandable microspheres in which a polymer, obtained from a component con-

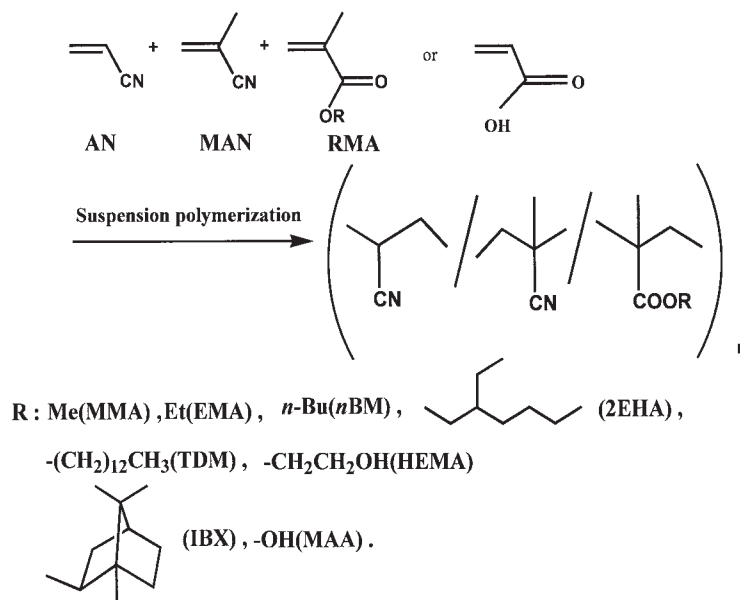
sisting of 80–97 wt % nitrile-containing monomers, 3–20 wt % non-nitrile-containing monomers, and 0.1–1 wt % trifunctional crosslinking agent, is used to microencapsulate a volatile expanding agent. The thermoplastic expandable microspheres obtained with this method are superior in heat resistance, and this means that the polymer cannot be expanded at 140°C or less.

For the development of excellent microspheres, the selection of a gas-proof polymeric composition, the balancing of the softening point and melt viscosity of the shell polymer, and the molecular structure and boiling point of the blowing agent are important. Furthermore, during heat exposure, the ductility and intensity of the shell are also dominant factors.<sup>3</sup> For this reason, a monomer with gas-barrier properties such as acrylonitrile (AN) or methacrylonitrile (MAN) is generally used as a polymerizable monomer.<sup>11–14</sup>

However, very little work is currently available in the published literature on the correlation between the polymer structure parameters and heat resistance in the field of thermoplastic microspheres.

The objective of this study was to clarify the relationship between four polymer structure parameters: the cohesive energy density ( $e_{\text{coh}}$ ), the free volume, the glass-transition temperature ( $T_g$ ), and the heat resistance of thermoplastic expandable microspheres. These parameters can be obtained easily by the group contribution method, except for acidic polymers. In

Correspondence to: T. Oishi (oishi@yamaguchi-u.ac.jp).



Scheme 1 Thermoplastic expandable microspheres.

the field of polymer membranes, many researchers have presented the application of a correlation between the molecular structures and gas permeability to barrier material selection. It seems that a group contribution method is the most suitable for achieving the stated objective, and several such approaches have been used for the correlation or prediction of gas permeability coefficients of polymers.<sup>15–19</sup> Group contribution methods are commonly employed to calculate specific properties of polymers, and details of this methodology have been summarized by Van Krevelen.<sup>20</sup> To clarify the cohesive property of the substance, the cohesive energy is generally measured.  $e_{\text{coh}}$  is one of the most important parameters for gas-barrier properties.

In an attempt to relate the penetration to the polymer, Lee<sup>21</sup> put forward a prediction technique for gas permeability from the polymer structure on the basis of a specific-free-volume (SFV) diffusive theory. A functional-free-volume (FFV) diffusive theory by Park and Paul<sup>22</sup> is better than the SFV diffusive method in predicting gas permeability because the FFV method was modified by Park and Paul to achieve the desired predictive capability.

Therefore, we synthesized various thermoplastic expandable microspheres, as shown in Scheme 1. The expandable properties of the resulting thermoplastic expandable microspheres were investigated for correlation with the polymer structure parameters.

## EXPERIMENTAL

### Materials

All the monomers, solvents, and reagents, except for dipentaerythritol hexaacrylate (DPE) and colloidal sil-

ica dispersion, were purchased from Wako Pure Chemical Industries Co., Ltd. (Tokyo, Japan). DPE was purchased from Kyoeisha Chemical Co., Ltd. (Osaka, Japan). Colloidal silica dispersion in water was purchased from Asahidenka Industries Co., Ltd. (Osaka, Japan).

### Polymerization procedure for the thermoplastic microspheres

A polymerization reactor (500 mL) equipped with an agitator was charged with 155 g of deionized water, 55 g of sodium chloride, and 40 g of 20 wt % colloidal silica dispersion in water. To this mixture was added 0.5 g of a 36 wt % aqueous solution of poly(vinyl pyrrolidone). A solution (0.4 g) containing 10 wt % sodium nitrite was added. The pH of the aqueous solution was adjusted to 3–4 with hydrochloric acid. AN and MAN were used as the nitrile-containing monomers. To clarify the relationship between the polymer structure and expandable properties, we used several non-nitrile-containing monomers—seven kinds of methacrylic acid (MAA) derivatives, MAA, and acrylic acid (AA)—as the third monomer. The seven MAA derivatives were methyl methacrylate (MMA), ethyl methacrylate (EMA), *n*-butyl methacrylate (BMA), 2-ethyl hexyl methacrylate (2EHA), tridecyl methacrylate (TDM), 2-hydroxyethyl methacrylate (HEMA), and isobornyl methacrylate (IBX).

Additionally, DPE was used as the crosslinking agent. The experiments were carried out with different molar ratios of the various monomers. An oil-phase mixture was prepared with 85 g of the monomer and contained 20 wt % blowing agents (*n*-pentane/*n*-hexane) and 1 g of 2,2'-azobisisobutyronitrile (AIBN) as

TABLE I  
Effect of the Content and Species of Nonnitrile Monomer on the Polymerizations  
of Thermoplastic Microspheres for 15 h at 60°C<sup>a</sup>

Run	Nitrile monomer		Non-nitrile monomer		Crosslinking agent	Blowing agent			Yield (wt %) <sup>b</sup>	Particle size (μm) <sup>c</sup>	T <sub>start</sub> (°C)	T <sub>max</sub> (°C)	D <sub>max</sub> (μm)
	AN (wt %)	MAN (wt %)	Name	wt %	DPE (wt %)	C <sub>5</sub> H <sub>12</sub> (wt %)	C <sub>6</sub> H <sub>14</sub> (wt %)						
1	68	32	MMA	0	0.0174	14.8	5.7	75.7	37.2	122	169	342	
2	67	32		1	0.0174	14.8	5.7	84.9	31.3	135	169	580	
3	63	32		5	0.0174	14.8	5.7	85.5	33.9	129	166	611	
4	58	32		10	0.0174	14.8	5.7	83.2	34.8	118	162	630	
5	67	32	EMA	1	0.0174	14.8	5.7	82.3	30.1	134	169	553	
6	63	32		5	0.0174	14.8	5.7	85.8	33.8	122	164	399	
7	58	32		10	0.0174	14.8	5.7	83.2	30.2	114	143	368	
8	67	32	BMA	1	0.0174	14.8	5.7	85.7	34.4	132	169	510	
9	63	32		5	0.0174	14.8	5.7	86.4	33.2	123	164	514	
10	58	32		10	0.0174	14.8	5.7	87.1	29.4	118	150	395	
11	67	32	2EHA	1	0.0174	14.8	5.7	87.0	34.1	134	170	478	
12	63	32		5	0.0174	14.8	5.7	86.2	33.3	124	163	465	
13	58	32		10	0.0174	14.8	5.7	86.1	26.8	129	150	187	
14	67	32	TDM	1	0.0174	14.8	5.7	83.1	31.8	137	169	662	
15	63	32		5	0.0174	14.8	5.7	87.6	34.6	133	166	504	
16	58	32		10	0.0174	14.8	5.7	87.1	30.6	155	164	173	
17	67	32	HEMA	1	0.0174	14.8	5.7	83.0	38.0	133	170	632	
18	63	32		5	0.0174	14.8	5.7	82.7	32.6	136	166	620	
19	58	32		10	0.0174	14.8	5.7	82.2	28.5	136	163	452	
20	67	32	IBX	1	0.0174	14.8	5.7	84.5	35.7	131	170	632	
21	63	32		5	0.0174	14.8	5.7	86.2	37.5	127	167	522	
22	58	32		10	0.0174	14.8	5.7	88.5	27.8	123	161	388	
23	67	32	MAA	1	0.0174	14.8	5.7	79.7	31.0	140	170	585	
24	63	32		5	0.0174	14.8	5.7	78.9	31.4	139	172	541	
25	58	32		10	0.0174	14.8	5.7	83.4	39.5	129	178	764	
26	54.4	25.6		20	0.0174	14.8	5.7	84.2	45.2	145	195	1232	
27	47.7	22.3		30	0.0174	14.8	5.7	84.0	41.3	161	219	928	
28	34.0	16.0		50	0.0174	14.8	5.7	88.2	59.6	201.5	230	36.5	
29	58	32	AA	10	0.0174	14.8	5.7	85.5	41.5	127	170	709	
30	54.4	25.6		20	0.0174	14.8	5.7	82.6	63.1	125	171	554	

<sup>a</sup> Initiator = AIBN, [AIBN]/[monomer] = 0.008.

<sup>b</sup> Based on the total amount of monomer (g).

<sup>c</sup> As measured by a laser-scattering method.

an initiator. The oil-phase mixture was added to the water phase with violent agitation supplied by a blade rotating at a speed of about 10,000 rpm. The reactor was immediately sealed, and a portion was sampled to determine the particle size. The droplets appeared to have diameters of approximately 10–18 μm. After the initial dispersion, the reaction mixture was maintained at a temperature of about 60°C for a period of 15 h. At the end of this period, the temperature was lowered. The beads were filtered and subsequently dried in an air oven at a temperature of approximately 40°C.

#### Determination of the expandable properties with thermomechanical analysis (TMA)

To obtain the expandable properties, we measured expansion curves of the microspheres with temperature-ramping experiments (5°C/min.) with TMA

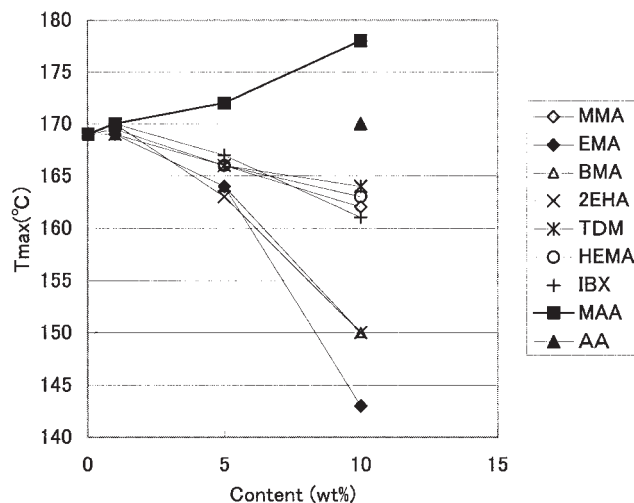
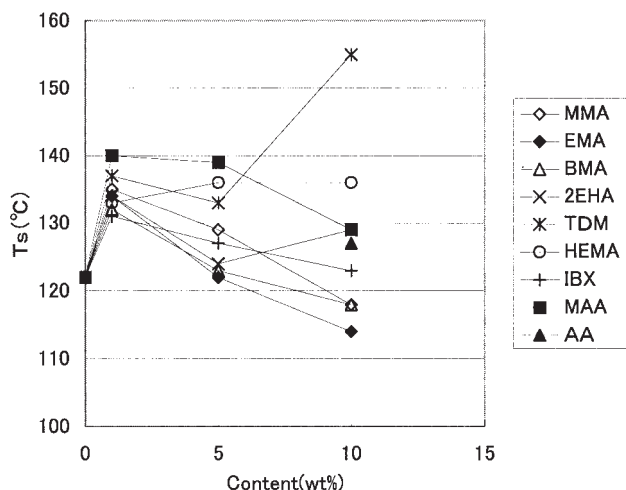


Figure 1 Effects of the addition of each non-nitrile monomer on T<sub>max</sub>.



**Figure 2** Effects of the addition of each non-nitrile monomer on  $T_g$ .

(TMA2940, TA Instruments, Inc., New Castle, DE). A sample (24  $\mu\text{g}$ ) was put into a cup and heated at a set speed (5°C/min.). When the spheres started to expand, a probe measured the movement. The temperature at which the expansion starts is called  $T_s$  (measured by TMA), whereas the temperature at which the maximum expansion is reached is called  $T_{\text{max}}$  (measured by TMA). The dimension change at which the maximum expansion is reached is called  $D_{\text{max}}$  (measured by TMA).

### Particle diameter distribution

The particle diameter distribution was measured with a Horiba LA-910 particle-diameter-distribution meter (Hariba Instruments, Inc., Kyoto, Japan).

### Evaluation of the polymer structure parameters

#### FFV

This parameter was estimated by the group contribution method of Park and Paul.<sup>22</sup> FFV was defined as follows:

$$\text{FFV} = (V - V_0)/V$$

where  $V$  is the volume of the polymer at 298 K and  $V_0$  is the volume occupied by the polymer chains.  $V$  is defined as

$$V = \sum_{k=1}^K \beta_k (V_w)_k$$

where  $(V_w)_k$  is the van der Waals volumes of the various groups in the polymer structure,  $\beta_k$  is the

empirical factor, and  $K$  is the total number of groups into which the repeat unit structure of the polymer is divided.

This term can be calculated by Bondi's group contribution method<sup>16</sup> as follows:

$$V = 1.3 \sum_{k=1}^K (V_w)_k$$

The factor of 1.3 was estimated by Bondi from the packing densities of molecular crystals at absolute zero and accounts for the fact that this volume is greater than the molecular volume.

#### $e_{\text{coh}}$

This parameter was calculated by the group contribution method of Hoftyzer and Van Krevelen.<sup>23</sup> The cohesive energy per unit of volume is called  $e_{\text{coh}}$ .

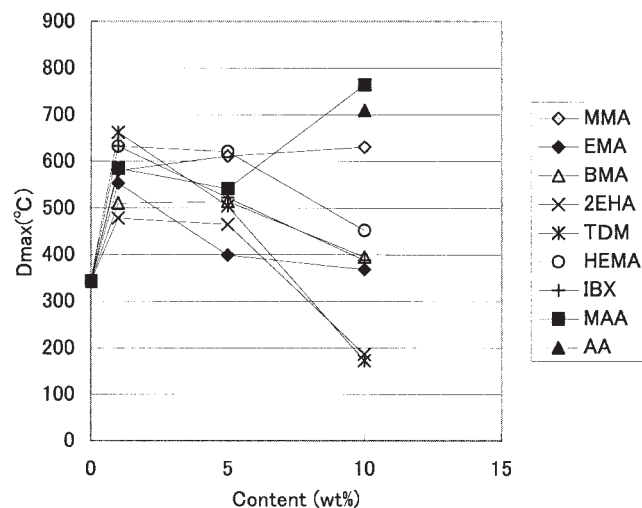
#### $T_g$

This parameter was taken from *Polymer Handbook*.<sup>24</sup>

## RESULTS AND DISCUSSION

### Syntheses of the microspheres

The relationship between the composition ratios of AN, MAN, and a non-nitrile monomer and the expandable properties was investigated and is summarized in Table I. The concentrations of each non-nitrile monomer with respect to the nitrile monomers were 0, 1, 5, and 10 wt %. However, the concentrations of MAA were 1, 5, 10, 20, 30, and 50 wt %. The range of particle sizes obtained within the limits of 0–10 wt %



**Figure 3** Effects of the addition of each non-nitrile monomer on  $D_{\text{max}}$ .

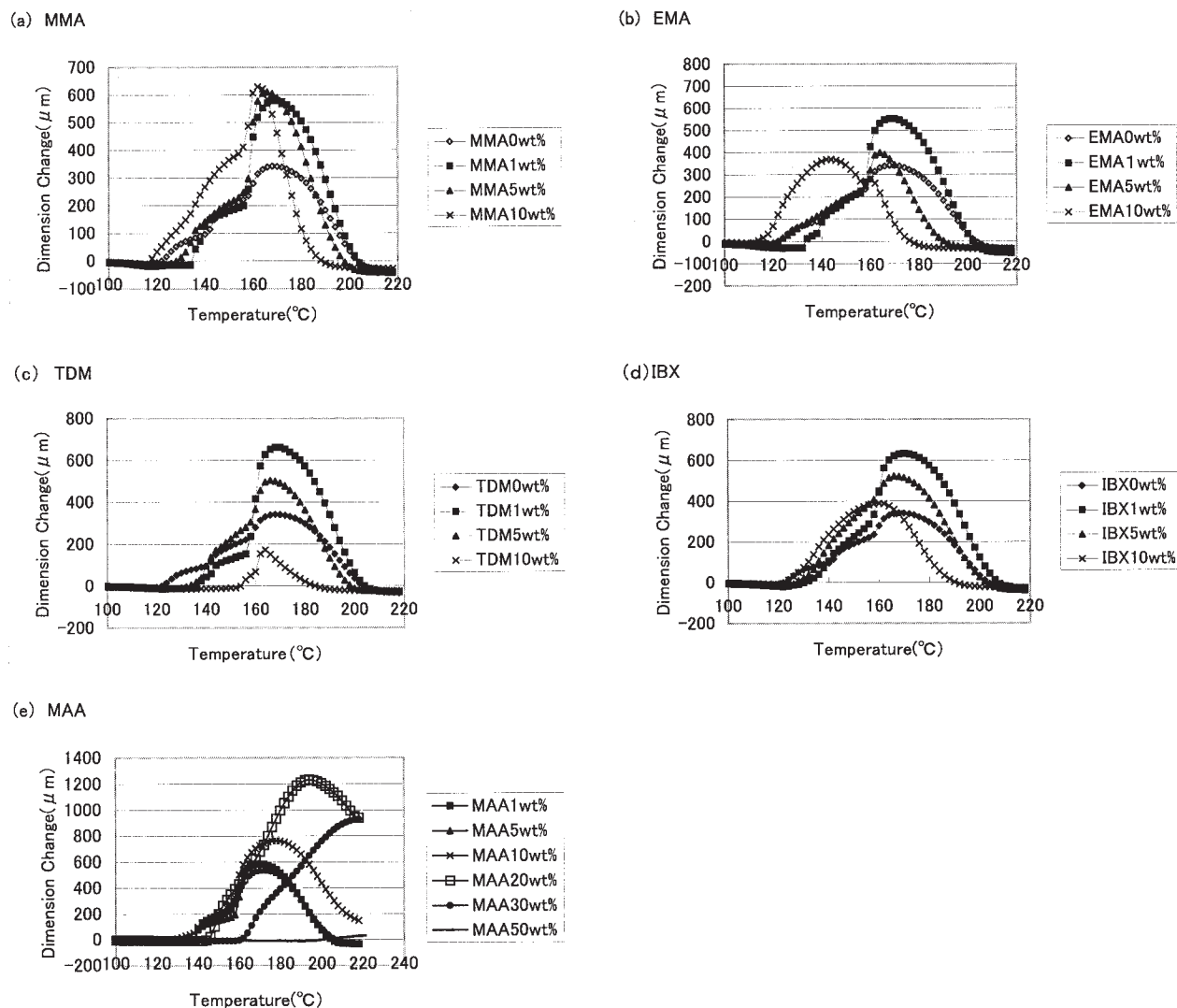


Figure 4 TMA curves for the addition of each non-nitrile monomer.

non-nitrile monomer was 26.8–39.5  $\mu\text{m}$ . From 20 to 50 wt % MAA, the particle sizes were larger than the others. This was probably due to higher hydrophilicity.

The yields were 75–88 wt %, and they decreased with higher hydrophilic monomers.

#### Relationship between the polymer structure parameters and expandable properties

A series of experiments was conducted to examine the effects of the polymer structure parameters on the expandable properties, particularly the heat resistance. The results are summarized in Table I, and the effects of the addition of each monomer on  $T_{\text{max}}$ ,  $T_s$ , and  $D_{\text{max}}$  are shown in Figures 1–3. A typical TMA curve for the effect of the addition of MMA is shown in Figure 4(a). The microspheres prepared with the addition of 1 wt % monomer in this experiment

showed higher  $D_{\text{max}}$  values than those prepared with only the nitrile monomer and excellent heat resistance, as shown in Figures 3 and 4(a–e).

$D_{\text{max}}$  decreased with the addition of larger amounts of the other monomer, except for MAA, as shown in Figure 3. Moreover,  $D_{\text{max}}$  for MAA derivatives decreased when the alkyl chain became long. The effects of the addition of MAA derivatives on  $T_{\text{max}}$  and  $T_s$  indicated different tendencies in Figures 1, 2, and 4. Figure 4(b,c) shows the TMA curves for samples with EMA and TDM added. Adding EMA led to the lowest  $T_{\text{max}}$  and  $T_s$  values in this series. Adding TDM did not lead to low  $T_{\text{max}}$  and  $T_s$  values. The reason for this expandable behavior of EMA could not be explained. For TDM, crystallinity was apparently involved for the expandable properties.

Japanese patent 5-285376 (1993) describes a method of producing thermoplastic expandable microspheres

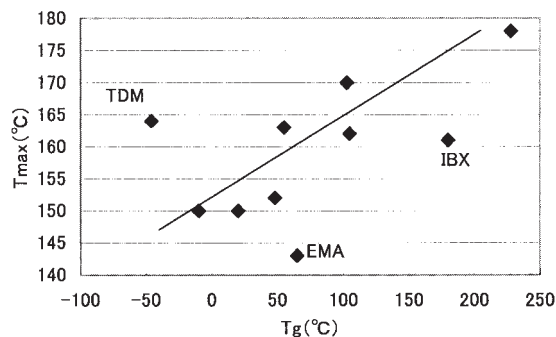


Figure 5 Relationship between  $T_g$  and  $T_{max}$ .

that are particularly excellent with respect to heat resistance. The application of a monomer that can produce a homopolymer with a high  $T_g$  is effective. Such monomers include MAN, acrylamide, MAA, and salts thereof, IBX, dicyclopentenyl acrylate, and so on. However, as shown in Figures 1, 4(d), and 5, an increase in  $T_{max}$  could not be obtained with the addition of IBX. An IBX concentration greater than 5 wt % led to a tendency for  $T_{max}$  and  $D_{max}$  to decrease. Figure 5 shows a correlation line between the polymer  $T_g$  values of the non-nitrile-containing monomers and the  $T_{max}$  values obtained by the addition of the non-nitrile-containing monomers. The  $T_{max}$  values of IBX, EMA, and TDM exhibited deviations from the line. If  $T_{max}$  plays a role in the gas diffusivity with the polymer structure, the effects of various molecular structure parameters, such as the polarity, hydrogen bonding,  $e_{coh}$ , and FFV, on the diffusion constant should be considered. The results for IBX may be due to relatively low  $e_{coh}$  and FFV values, as shown in Table II.

TABLE II  
Properties of the Polymers

Polymer	$T_g$ (°C) <sup>a</sup>	1/FFV (g/cc) <sup>b</sup>	$e_{coh}$ (J/cm <sup>3</sup> ) <sup>c</sup>
PAN	105	14.80	1116
PMAN	120	10.30	662
PMMA	105	8.34	386
PEMA	65	7.22	367
PBMA	20	5.83	330
P(2EHA)	-10	6.83	325
PTDM	-46	6.30	317
PIBX	180	6.17	260
PHEMA	55	7.36	795
PMAA	228		486
PAA	103		609

PMMA = poly(methyl methacrylate); PEMA = poly(ethyl methacrylate); P(2EHA) = poly(2-ethyl hexyl methacrylate); PTDM = poly(tridecyl methacrylate); PIBX = poly(isoborynyl methacrylate).

<sup>a</sup> Polymer Handbook.<sup>24</sup>

<sup>b</sup> Park–Paul method.

<sup>c</sup> Hoftyzer–Van Krevelen method.

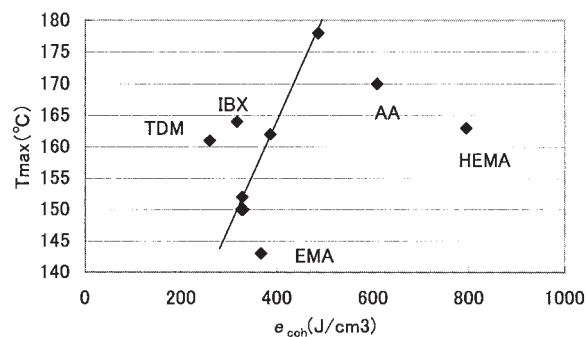


Figure 6 Relationship between the polymer  $e_{coh}$  and  $T_{max}$  values.

HEMA and AA, having relatively high  $e_{coh}$  values, as shown in Table II, also showed low  $T_{max}$  values, as shown in Figures 1 and 6. This reason may be ascribed lower  $T_g$  and FFV values.

The results clearly show that the microspheres of runs 23–25, prepared with MAA, had higher  $T_{max}$ 's than those prepared with the others. Additionally, with higher concentrations of MMA (20, 30, and 50 wt %),  $T_{max}$  increased for runs 26–28 in Figure 4(e). Many characteristics of polymers depend primarily on weak intermolecular forces rather than on strong covalent forces along the polymer chains. In most common polymers, the molecules are held together by weak van der Waals forces of the dispersion or dipolar type. In some cases, such as poly(methacrylic acid) (PMAA), poly(acrylic acid) (PAA), and poly(2-hydroxyethyl methacrylate) (PHEMA), the intermolecular forces are enhanced by hydrogen bonding. For PMAA and PAA, the force is also enhanced by electrostatic interactions for behavior as a polyelectrolyte. Electrostatic interactions are known to be the strongest. FFV for PMAA and PAA cannot be determined because an occupied volume for acid polymers with COOH groups cannot be estimated according to the group contribution method.<sup>20</sup> However, FFV of PMAA and PAA can exhibit the same level as polymethacrylonitrile (PMAN) and polyacrylonitrile (PAN) or better.

On the basis of these considerations, it may be concluded that the parameters due to an increase in  $T_{max}$  were strong intermolecular forces such as hydrogen bonding and electrostatic interactions, high  $e_{coh}$  values, low FFV values, and high  $T_g$  values. Copolymerization with a monomer containing a COOH group with a relatively high  $T_g$  value, such as MAA, is most suitable for the formation of heat-resistant microspheres.

## CONCLUSIONS

The effects of the addition of non-nitrile-containing monomers on the heat resistance of thermoplastic ex-

pandable microspheres containing AN and MAN were investigated. The results suggested that the addition of an acidic monomer with relatively strong intermolecular forces and a high  $T_g$  value, such as MAA, was suitable for the formation of heat-resistant microspheres.

The authors are grateful to Kuwahara, head of the specialty chemicals division of Sekisui Chemical Co., Ltd. (Tokyo, Japan), and to Adachi and Kake, president and managing director, respectively, of Tokuyama Sekisui Co., Ltd. (Yamaguchi, Japan), for permitting and supporting the publication of this work.

## References

1. Huang, Y.; Dimonie, V. L.; Klein, A. *Emulsion Polym Inst Graduate Res Prog Rep* 2004, 61, 161.
2. Nakajima, T. *Nippon Gomu Kyoukaishi* 2001, 74, 412.
3. Kida, S. *Kobunshi* 1991, 40, 248.
4. Klas, E. *Blowing Agents Foaming Proc* 19–20 May, 2003, 17.
5. Kostrzewa, M.; Molenda, J.; Prot, T. *Int Polym Sci Technol* 2000, 27, 91.
6. Morehouse, D. S. U.S. Pat. 3,615,972 (1971).
7. Yokomizo, T.; Tanaka, K.; Niinuma, K. *Jpn. Kokai Tokkyo Koho JP 5-15499* (1993).
8. Kida, S.; Kitano, K.; Oino, S. *Jpn. Kokai Tokkyo Koho JP 5-285376* (1993).
9. Yokomizo, T.; Tanaka, K. *Jpn. Kokai Tokkyo Koho JP 2894990* (1999).
10. Kron, A. *Eur Pat. EP 1 149 628 A1* (2001).
11. Ejiri, T.; Satake, Y. *Jpn. Kokai Tokkyo Koho JP 2000-191817* (2000).
12. Hara, M. *Plast Age* 2000, 46, 95.
13. Tabata, Y. *Konbatekku* 1998, 6, 36.
14. Teraoka, T. *Konbatekku* 1995, 3, 14.
15. Salame, M. *Polym Eng Sci* 1986, 22, 26.
16. Bondi, A. *Physical Properties of Molecular Crystals, Liquids and Glasses*; Wiley: New York, 1968.
17. Bondi, A. *J Polym Sci Part A: Gen Pap* 1964, 2, 3159.
18. Haward, R. N. *J Macromol Sci Rev Macromol Chem* 1970, 4, 191.
19. Jia, L.; Xu, J. *Polym J* 1991, 23, 417.
20. Van Krevelen, D. W. *Properties of Polymers*, 3rd ed.; Elsevier: Amsterdam, 1990.
21. Lee, W. M. *Polym Eng Sci* 1980, 1, 20.
22. Park, J. Y.; Paul, D. R. *J Membr Sci* 1997, 23, 125.
23. Hoftyzer, P. J.; Van Krevelen, D. W. *Properties of Polymers*, 2nd ed.; Elsevier: Amsterdam, 1976.
24. Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989.