Colloid Polym Sci (2004) 283: 111–116
DOI 10.1007/s00396-004-1190-4

SHORT COMMUNICATION

Takuji Okaya
Kenji Kikuchi
Atsushi Suzuki
Chika Ohara

Thermosensitive poly(methyl methacrylate) emulsion prepared in the presence of poly(vinyl alcohol) with a cloud point as a protective colloid

Received: 12 February 2004
Accepted: 14 July 2004

T. Okaya (✉) · K. Kikuchi
A. Suzuki · C. Ohara
Department of Materials Science,
School of Engineering,
The University of Shiga Prefecture,
2500 Hassaka, 522-8533 Hikone, Japan
E-mail: okaya@mat.usp.ac.jp
Tel.: +81-749-288368
Fax: +81-749-288590

Abstract An emulsion of poly(methyl methacrylate) (PMMA) was prepared using poly(vinyl alcohol) (PVA) of low degree of hydrolysis with a cloud point as a protective colloid. The behaviour of an aqueous solution of PVA with 80% degree of hydrolysis was first investigated in terms of the Huggins constant in viscometry. MMA was polymerized using the PVA at 20 °C, where no abnormality in the aqueous PVA was observed. The change in transmittance of the emulsion observed with a UV–vis photometer revealed that in the case of UV light of wavelength 370 nm, the transmittance decreased markedly at around 30 °C with an increase in temperature, and then increased with a decrease in temperature. The thermosensitive property resulted from PVA with a low degree of hydrolysis with a cloud point, at a higher temperature of which the PVA loses solubility in water owing to weakening of the hydrogen bond between PVA molecules and water.

Keywords Emulsion polymerization · Thermosensitive emulsion · Methyl methacrylate · Poly(vinyl alcohol) · Cloud point

Introduction

Poly(vinyl alcohol) (PVA) has been used in emulsion science and industry as a polymeric protective colloid. The degree of hydrolysis of PVA is 88% or higher, i.e., residual acetyl groups represent 12 mol % or less. Although PVA with a lower degree of hydrolysis, for example, 80%, has been produced commercially, it has not found application for surface-active reagents in polymer emulsions. The reason must be due to the phase separation that is characteristic of the aqueous solution of this PVA. Nord et al. [1] reported that an aqueous solution of commercial PVA with a degree of hydrolysis of 82% showed phase separation at temperatures higher than 23 °C. This phenomenon is well-known in physical chemistry as the lower critical solution temperature. The temperature called the cloud point is caused by the weakening of the hydrogen bond between the PVA molecules and water at higher temperatures. With a decrease in the strength of the hydrogen bond that enables PVA molecules to be soluble in water, the solubility of the PVA in water decreases and results in precipitation of the PVA molecules. An aqueous solution of commercial PVA with 80% degree of hydrolysis becomes turbid at about 40 °C [2].

If emulsion polymerization is carried out at a temperature lower than the cloud point of PVA, the polymer emulsion obtained might show thermosensitive properties at temperatures higher than the cloud point, resulting in the coagulation of the emulsion particles caused by loss of protective colloid ability of the PVA. When the polymer in the particles has a much higher T_g than the cloud point of the PVA, the emulsion may be regenerated by lowering the temperature of the aggregated emulsion to a temperature below that of the cloud point. Thus, the emulsion is expected to be a kind of thermosensitive one. Two types of thermosensitive emulsions appear to have been reported: one consists of the polymers in the particles being thermosensitive, such as poly(*N*-isopropylacrylamide) [3, 4], poly(*N*-alkylmethacrylamide) [5, 6, 7], and their copolymers [8, 9]; the other consists of the thermosensitive hairy polymers on the particle surfaces [10, 11]. These thermosensitive emulsions are interesting from the biological point of view. However, there seem to be no papers concerning thermosensitive emulsions using PVA as a polymer protective colloid.

We have been studying the emulsion polymerization of methyl methacrylate (MMA) using normal PVA as a polymer protective colloid [12, 13, 14, 15]. Grafting of MMA onto PVA took place remarkably in the model emulsion polymerization using low amounts of MMA. Utilizing the results of these studies, we tried to produce a thermosensitive poly(MMA) (PMMA) emulsion using PVA with cloud point instead of normal PVA.

Experimental

Materials

PVA was supplied by Kuraray (PVA-1: PVA-217, degree of hydrolysis 88%, degree of polymerization 1,750; PVA-2: PVA-420, degree of hydrolysis 80%, degree of polymerization 2,000). MMA (Wako Pure Chemical Industries) was used after distillation under reduced pressure. Water was distilled after ion-exchange. Hydrogen peroxide (24.3% aqueous solution), ferrous sulfate ($7H_2O$), and sodium formaldehyde sulfoxylate (Rongalite) were supplied from Nacalaitesq and were used as received. Ammonium persulfate (APS, Wako Pure Chemical Industries) of general reagent grade was used as received.

Emulsion polymerization

Prescribed amounts of PVA were added to a 100-mL flask equipped with an argon inlet tube, a vacuum-pumping cock, a cock to add reagents, and a sampling cock. An evacuation-argon introduction procedure was carried out three times. Water and MMA, after being deaerated with argon, were added to the reactor. A magnetic stirrer was set in the flask. Conversion was measured gravimetrically.

Fractionation of the polymers

The polymers in the emulsion were fractionated into acetone-soluble, water-soluble, and insoluble parts. Each part was regarded as homo-PMMA, nongrafted PVA, and graft polymer, respectively.

Measurement

The viscosities of PVA were measured in water at 20 and 30 °C using Ubbelohde type viscometers. Intrinsic viscosities and Huggins constants were determined with the following two equations.

– Huggins equation:

$$\eta_{\mathrm{sp}}/C = [\eta] + k'[\eta]^2 C. \tag{1}$$

– Schulz–Blaschke's equation:

$$\eta_{\mathrm{sp}}/C = [\eta] + k'[\eta]\eta_{\mathrm{sp}}. \tag{2}$$

The particle diameter was measured by a dynamic light scattering method (Otsuka Electronics, DLS-PAR-3). The degree of polymerization of homo-PMMA was measured by gel permeation chromatography (Toso, $\mathrm{TSK_{gel}}$, $\mathrm{GMH_{HR}}$-M, polystyrene standard). The transmittance of the emulsion was measured with a spectrophotometer (Hitachi, model 200-20) using wavelengths of 700 (10-mm cell thickness) and 370 nm (1-mm cell thickness).

Results and discussions

Investigation of the behaviour of the PVA aqueous solution at 20 and 30 °C

To determine the preferable polymerization temperature, the behaviour of the PVA aqueous solution was investigated at 20 and 30 °C in terms of the Huggins constant calculated in viscometry. The relation between η_{sp}/C and PVA concentration, Huggins plot, is shown in Fig. 1. Viscometry was carried out for PVA-1 and PVA-2. The relation between η_{sp}/C and η_{sp}, Schulz–Blaschke plot, is shown in Fig. 2, using the same data as in Fig. 1. The intrinsic viscosities and Huggins constants are listed in Table 1. The latter were calculated from slopes in Figs. 1 and 2 using Eqs. (1) and (2). The intrinsic viscosities and Huggins constants obtained from Eqs. (1) and (2) are shown with subscripts H and S, respectively.

In general, the Huggins equation has been widely used in viscometry to determine molecular weights of polymers. However, Ibrahim [16] pointed out that there might be mathematical errors in the Huggins equation given in Eq. 1) that are brought about by neglecting the third and higher terms on the right-hand side in the original Huggins, Eq. 3) that is equivalent to the Schulz–Blaschke equation.

$$\eta_{\mathrm{sp}}/C = [\eta]\left[1 + k'[\eta]C + (k'[\eta]C)^2 + (k'[\eta]C)^3 + \ldots\right] \tag{3}$$

One of the authors investigated the viscometry of a PVA aqueous solution from this point of view, and found that Eq. (1) did not bring about large errors in the

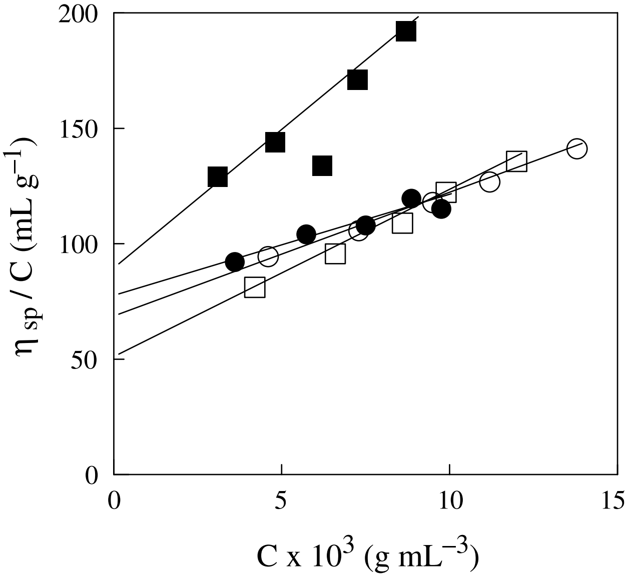

Fig. 1 Relation between concentration and η_{sp}/C of poly(vinyl alcohol) (*PVA*) aqueous solutions (Huggins plots). PVA-1 (*circles*); PVA-2 (squares); 30 °C (*open circles*); 20 °C (*solid circles*)

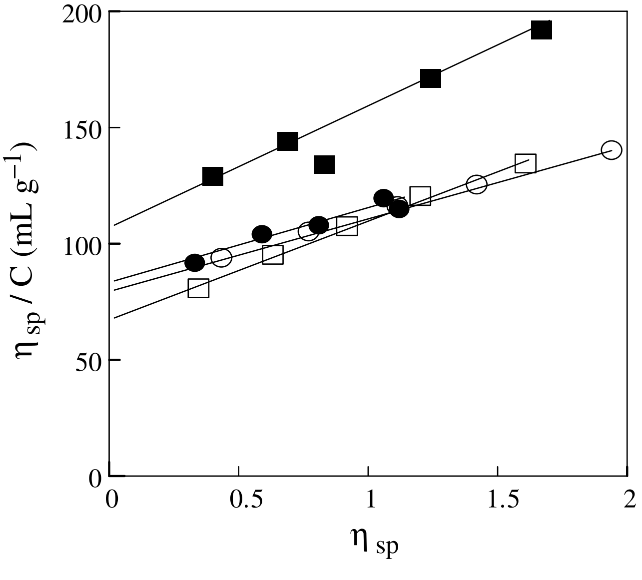

Fig. 2 Relation between η_{sp} and η_{sp}/C of PVA aqueous solutions (Schulz–Blaschke plots) The *symbols* are as in Fig. 1

intrinsic viscosity; however, Huggins constants obtained from Eq. (1) contained large errors [17]. According to Yamakawa's theoretical calculation, the Huggins constant must be smaller than 0.5 [18]. Nevertheless the Huggins constants obtained from many viscometry data of the PVA–water system were much larger than 0.5. In contrast, Huggins constants obtained from the Schulz–Blaschke equation were less than 0.5 (0.48–0.42 with an increase in intrinsic viscosity) [17]. From this result, it is useful to check the Huggins constant obtained from the Schulz–Blaschke equation in the PVA–water system, when a type of PVA different from the ordinary one is to be used.

Table 1 Intrinsic viscosities and Huggins constants of poly(vinyl alcohol) (*PVA*) aqueous solutions

Sample	Temperature (°C)	Intrinsic viscosity (mL/g)		Huggins constant	
		$[\eta]_H$	$[\eta]_S$	k'_H	k'_S
PVA-1	30	72	80	0.90	0.43
	20	77	81	0.93	0.43
PVA-2	30	53	67	2.35	0.61
	20	85	108	1.31	0.51

As seen in Table 1, every Huggins constant obtained from Eq. (1), k'_H, was also much larger than 0.5, while those obtained from the Schulz–Blaschke equation, k'_S, were close to 0.5. Accordingly we adopt k'_S rather than k'_H to evaluate the behaviour of PVA in aqueous solution. The value of k'_S of 0.43 for PVA-1 at 20 and 30 °C indicates the ordinary value, while the values for PVA-2, 0.61 at 30 °C and 0.51 at 20 °C, seemed to be abnormal. The value of 0.51 is very close to the upper limit of 0.50 mentioned previously, while 0.61 is clearly larger than the ordinary value. This temperature range must be near the cloud point of PVA [1, 2]. On the basis of the behaviour of the aqueous solution of PVA with a cloud point, we decided to carry out the polymerization at 20 °C.

Emulsion polymerization at 20 °C

Emulsion polymerization of MMA was carried out using a redox initiator system composed of ferrous sulfate/hydrogen peroxide/(SFS, Rongalite). In a preliminary experiment, the emulsion was not stable enough during the polymerization using a system of 10 mL MMA in 100 mL water; therefore a lower content of MMA was adopted. The recipe was as follows: Initial MMA 1 mL (an additional 2 mL was added 90 min after the initiation), water 100 mL, PVA 1.0 g, $FeSO_4{\cdot}7H_2O$/water/SFS 0.1/2.0/4.0 (×2.21×10^{-3} mol/L, each).

The time–conversion curves of the emulsion polymerization using PVA-1 and PVA-2 as a protective colloid are shown in Fig. 3. In stage 1, where one thirds of the MMA was added, the conversions reached about 80% at 90 min. After adding residual amounts of MMA and hydrogen peroxide, polymerization was continued for 60 min (stage 2). The final conversions were approximately 80%. The particle diameters and the numbers of particles during the polymerization are shown in Fig. 4. In the very early stage, particles of

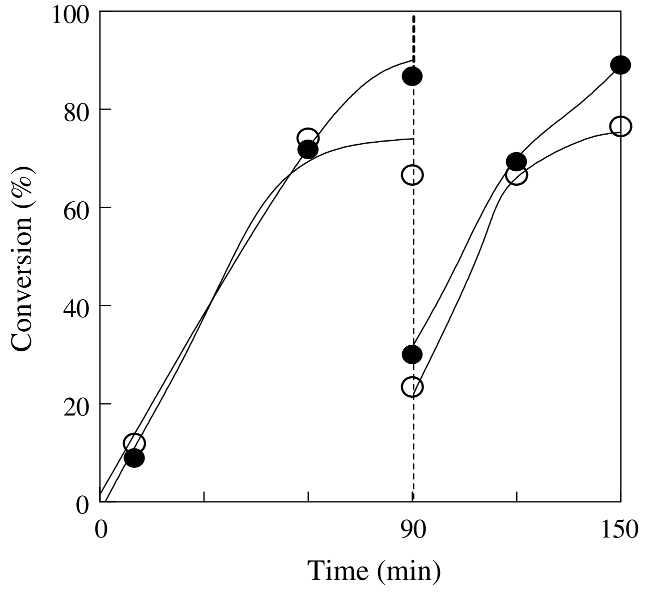

Fig. 3 Time–conversion curves of emulsion polymerization of methyl methacrylate (*MMA*). Recipe: MMA 1 mL added at time 0 min, and 2 mL added at time 90 min; water 100 mL; polymerization temperature 20 °C; Ferrous sulfate/Rongalite/hydrogen peroxide 0.1/2.0/4.0, (x2.21×10^{-3} mol/L). PVA-1 (*open circles*); PVA-2 (*solid circles*)

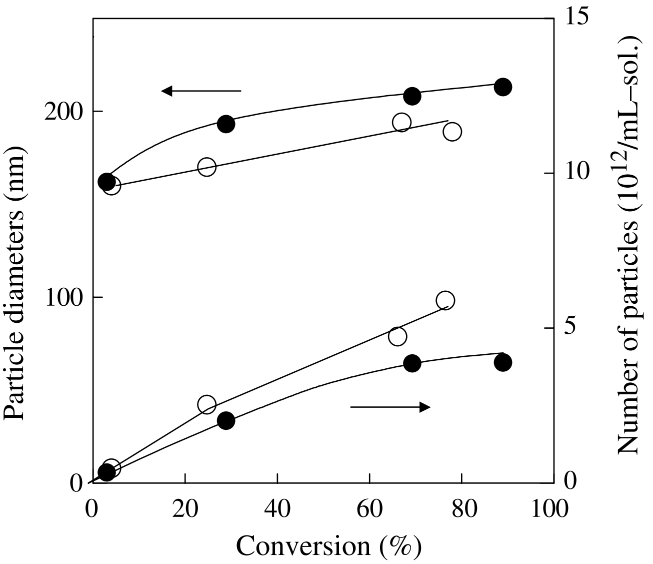

Fig. 4 Particle diameters and number of particles of poly(MMA) emulsions prepared as described in Fig. 3. PVA-1 (*open circles*); PVA-2 (*solid circles*)

about 160 nm were formed in both PVA systems, and became 190 and 210 nm at the last stage in the PVA-1 and PVA-2 systems, respectively. The number of particles kept increasing during the polymerization.

Grafting of MMA onto PVA was investigated by fractionation of the polymers in emulsions. The degrees of polymerization of homo-PMMA were measured. The data are listed in Table 2, where those of the emulsion polymerization at 60 °C with APS using PVA-1 are listed as a reference, although polymerization data are not shown. Grafting of MMA onto PVA occurred markedly in all cases, irrespective of the polymerization system. More than 90% of polymerized MMA was grafted, and more than 90% of PVA was also grafted. The amount of grafted PVA in PVA-1 may be slightly smaller than that in PVA-2, especially in stage 1. This may indicate weak reactivity of the vinyl acetate portion in PVA to the hydroxyl radical. On the other hand, the degree of polymerization of PMMA showed a large difference. It was 1,800 in the APS system, while it was 680 and 440 in the redox system. This might be due to the high rate of initiation in the latter system, although the rate of polymerization was rather low, partly because the propagation rate constant was lower. The difference in the particle diameters in both cases might have arisen from the difference in the degrees of polymerization of grafted PMMA that could be regarded as almost the same as homo-PMMA.

Evaluation of thermosensitivity of the emulsions

The transmittance of the emulsions given in Table 2 was measured with a UV–vis spectrometer between 20 and 80 °C. The emulsions were diluted to 1/80, and measured using a 10-mm cell at 700-nm wavelength so as to enhance the transmittance of the light. The change in transmittance with temperature is shown in Fig. 5. The measurement was done first with an increase and next with a decrease in temperature, and the temperature was kept for 5 min after every 5 °C change. The transmittance of the PVA-1 system remained constant during the measurement within experimental error, while that of the PVA-2 system decreased with an increase in temperature and recovered to the original transmittance with a decrease in temperature. The phenomenon seemed to exhibit the thermosensitivity, although it is not strong.

To make clearer the tendency, the measurement was carried out at higher particle concentration (the original emulsions being diluted to one eigth), using a 1-mm cell and a wavelength of 370 nm. The results are shown in Figure 6. The transmittance of the PVA-1 system did not change. In contrast there was a remarkable change in that of the PVA-2 system. With an increase in temperature the transmittance decreased markedly after 25 °C and slowly became almost constant. With a decrease in temperature after this, the transmittance recovered to some extent, but the recovery was not enough. This clearly shows the thermosensitivity of the

Table 2 Characterization of the poly(methyl methacrylate) (*PMMA*) emulsion obtained

Initiator	Polymerization temperature (°C)	PVA	Particle size (nm)	Grafting (%)[a]		Degree of polymerization[d]
				Grafted PMMA[b]	Grafted PVA[c]	
Redox	20	PVA-1	180	98 (98)	92 (92)	680
		PVA-2	220	99 (87)	99 (82)	440
APS[e]	60	PVA-1	110	94	88	1,800

[a] Numbers in parentheses are the grafting (%) at stage 1

[b] Based on polymerized MMA

[c] Based on feed PVA

[d] Measured on homo-PMMA

[e] Shown as a reference (not reported here)

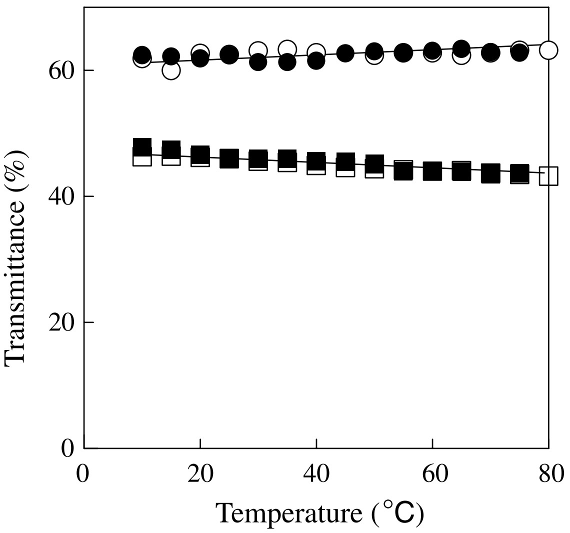

Fig. 5 Change in transmittance with temperature at 700 nm. Cell length 10 mm; PVA-1 (*circles*); PVA-2 (*squares*). *Open circles* represent an increase in temperature (kept for 5 min at each temperature); *solid circles* represent a decrease in temperature (kept for 5 min at each temperature)

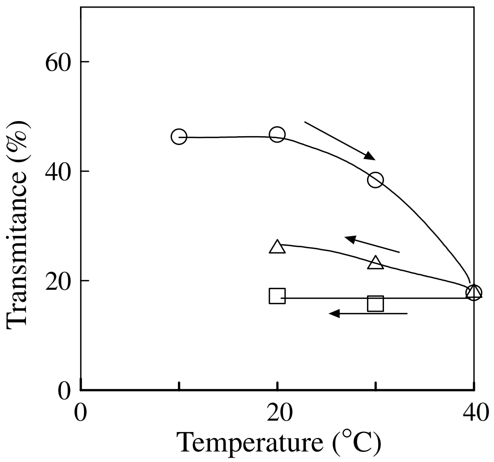

Fig. 7 Change in transmittance with change in temperature at 370 nm. Heated to the temperature (kept for 5 min at each temperature) (*circles*), cooled to the temperature for half an hour after being heated at 40 °C for 5 min (*squares*), cooled to the temperature for 3 h after being heated for 5 min (*triangles*)

emulsion using PVA with a cloud point as a protective colloid.

The decrease in transmittance at higher temperature must be due to the coagulation of the particles. Hydrophilicity of the PVA-2 molecules is weakened at higher temperature by the decrease of the strength of the hydrogen bond between PVA molecules and water. Consequently, the PVA-2 molecules on the surface of the particles lose the ability as a stabilizer causing the coagulation. According to scanning electron microscopy observations before and after heating to 40 °C, weak coagulation was observed after heating.

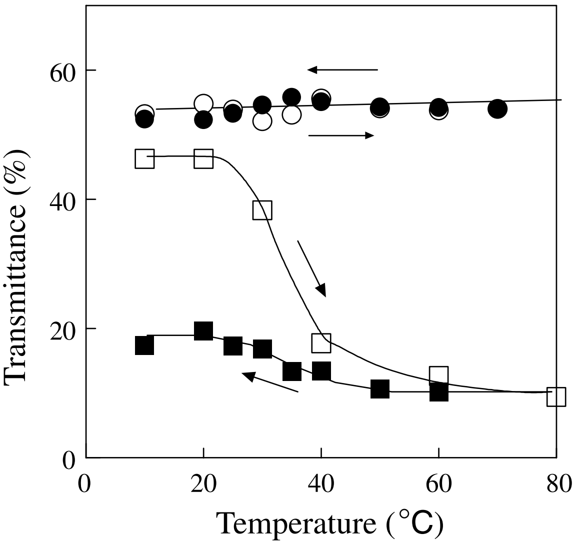

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Fig. 6 Change in transmittance with temperature at 370 nm. Cell length 1 mm; PVA-1 (*circles*); PVA-2 (*squares*). *Open circles* represent an increase in temperature (kept for 5 min at each temperature); *solid circles* represent a decrease in temperature (kept for 5 min at each temperature)

The ability of the stabilizer may be recovered when the emulsion is cooled to temperatures below the cloud point. The result shown in Fig. 6 shows the tendency to some extent, but the transmittance was much lower than the original one. The longer time might be necessary for the shrunken PVA molecules to recover enough hydrophilicity. Then we tried two cooling methods, as shown in Fig. 7. The temperature of the emulsion was elevated to 40 °C as described previously, kept there for 5 min, lowered to 30 °C, kept for half an hour (method 1) or 3 h (method 2), respectively, and finally kept at 20 °C for 30 min. The transmittance resulting from the application of method 1 showed little change, while that resulting from the use of method 2 recovery slightly, although it was still weak. If the coagulation is caused by the PVA molecules only and no coagulation between PMMA molecules in separate particles takes place, recovery might be more complete. Accordingly there may be coagulation between PMMA molecules in separate particles. Although the T_g of the particle polymer (PMMA) is 100 °C, residual monomer in the particles lowered the T_g, resulting in easier coagulation.

In this study, thermosensitivity of an emulsion using PVA with a cloud point as a protective colloid was observed. Clearer thermosensitivity might be needed to utilize the phenomenon, i.e., the recovery of the transmittance to the original value when the temperature is decreased from a temperature higher one than that of the cloud point.

References

1. Nord FF, Bier M, Timasheff SN (1951) J Am Chem Soc 73:289–293
2. Nagano K, Yamane S, Toyoshima K (1986) Poval, 2nd edn. Kobunshi Kankoukai, Kyoto, p 143
3. Pelton RH, Chibante P (1986) Colloid Surf 20:247
4. Meunier F, Elaissari A, Pichot C (1995) Polym Adv Technol 6:489
5. Kawaguchi H, Kawahara M, Yaguchi N, Hoshino F (1988) Polym J 20:903
6. Lowe JS, Chowdhry BZ, Parsonage JR, Snowdon MJ (1998) Polymer 39:1207
7. Duracher D, Elaissari A, Pichot C (1999) J Polym Sci Part A Polym Chem 37:1823
8. Duracher D, Elaissari A, Mallet F, Pichot C (2000) Macromol Symp 150:297
9. Fang S-J, Kawaguchi H (2002) Colloid Polym Sci 280:984
10. Kawaguchi H, Isono Y, Tsuji S (2002) Macromol Symp 179:75
11. Takata S, Shibayama M, Sasabe R, Kawaguchi H (2003) Polymer 44:495
12. Okaya T, Suzuki A, Kikuchi K (1999) Colloids Surf A 153:123
13. Okaya T, Suzuki A, Kikuchi K (2000) Macromol Symp 150:143
14. Okaya T, Suzuki A, Kikuchi K (2002) Colloid Polym Sci 280:188
15. Suzuki A, Yano M, Saiga T, Kikuchi K, Okaya T (2003) Prog Colloid Polym Sci 124:27
16. Ibrahim FW (1965) J Polym Sci Part A 3:469
17. Okaya T, Imai K (1979) Kobunshi Ronbunshu 36:329
18. Yamakawa H (1961) J Chem Phys 34:1360