A Novel Approach Using Differential Scanning Calorimetry to Investigate the Dissolved State in Aqueous Solutions of Polymers Used for Papermaking

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ABSTRACT: The size and conformations of dissolved polymer molecules of polyethylene glycol (PEG) in 5% aqueous solutions were examined through the use of differential scanning calorimetry (DSC). As long as the freezable bound water is considered to be the water enclosed by the entangled polymer chains in the solution, the appearance of the characteristics of a polymer begins to occur at a degree of polymerization (DP) between 11 and 21 and is largely completed at a DP of about 50. Assuming that the peak temperature of the DSC curve for the freezable bound water indicates the size of the entangled molecular coil, the lowering of the peak temperature with a decrease of molecular weight (MW) suggests a decrease in the size of the entangled molecular coil. The linear relationship between the peak temperature and the reciprocal of the number-average MW suggests melting point depression as a plausible mechanism for the peak temperature lowering. Mixing of two polymers with different MWs—and thus, entangled molecular coils of different sizes—causes a kind of polymer–polymer interaction and the coil sizes change as follows. If the difference in the values of the two MWs is large, the sizes of the entangled molecular coil of each MW are brought closer to each other. The extent of approach is roughly proportional to the mixing ratio. If the difference in the values of the two MWs is not large, the original entangled molecular coils disappear and a single molecular coil of intermediate size appears instead. The size of the single intermediate molecular coil varies roughly according to the simple mixing law for the values of the two MWs. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2798–2807, 2003

Key words: conformational analysis; degree of polymerization (dp); differential scanning calorimetry (DSC); water-soluble polymers; papermaking

INTRODUCTION

In modern papermaking a range of water-soluble polymers have been extensively used as additives.[1] To understand the role of such polymers it is very important to clarify the dissolved state of the polymer, using properties such as the molecular conformation in an aqueous solution, the manner in which the polymer is adsorbed onto fibers, and the degree to which the adsorbed polymer changes its molecular conformation during the consolidation of the paper web. However, almost no studies have been carried out on these points because of the lack of a method to investigate the dissolved state. In a previous study,[2] polyethylene glycol (PEG) was selected as a very flexible polymer that shows a random-coiled conformation in its aqueous solution. In that study the freezing behavior and the melting behavior of the solution were examined by use of differential scanning calorimetry (DSC). Two distinctive peaks in the DSC curve appeared during both cooling and heating. These peaks were attributed to the free water and freezable bound water. Further, the freezable bound water was concluded to be the water enclosed by the entangled PEG molecular chains. The percentage of freezable bound water was also found to increase linearly with an increase in the concentration of polymer. Thus, DSC was indicated as a plausible new method to investigate the degree of polymer chain entanglement in an aqueous solution. In the present study DSC curves for aqueous solutions of PEG having a series of molecular weights (MW) were examined to investigate the effects of MW and mixing of two MWs on the dissolved state.

EXPERIMENTAL

Differential scanning calorimetry

As in a previous study,[2] a Rigaku heat-flux–type differential scanning calorimeter 8240 B (Rigaku, Tokyo, Japan), equipped with a cooling cell, was used to determine the heating DSC curve. A given amount of sample aqueous solution, about 11 μL, was quantitatively transferred to the DSC aluminum sample pan, and then the aluminum lid was put on the sample to cover it. After weighing quickly, the pan was placed in
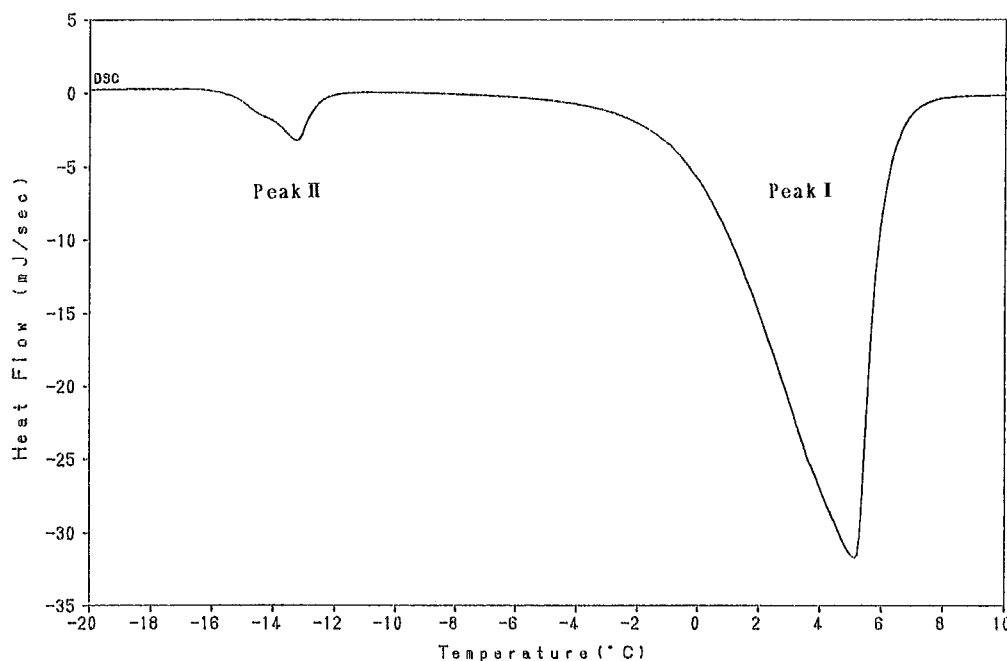
Figure 1 Heating DSC curve of aqueous PEG solution with M_n of 3500.

the DSC chamber and was promptly cooled below 0°C to minimize the evaporation of water from the gap between sample pan and lid. After further cooling to −45°C, the sample was then heated at a scanning rate of 2°C/min to room temperature. In the DSC heating curve, a small broad peak at about −10°C (peak II) and a large peak at about 0°C (peak I) were observed, as shown in Figure 1. The peak at the low-temperature side in each curve was attributed to the freezable bound water and the peak at the high-temperature side to the free water, as in the previous study.[2] In general there should be three kinds of water in the aqueous solution: nonfreezing water, freezable bound water, and free water. These three kinds were assigned to the water tightly bound to polymer molecules, the water enclosed by the entangled molecular chains, and the other water, respectively.[2] Thus, polymer chains with the enclosed water form a kind of domain within the solution. On lowering the temperature the water enclosed in the domain freezes at a temperature lower than the freezing temperature of free water, and the frozen water in the domain melts below the melting temperature of free water on elevating the temperature.

The amounts of free water and freezable bound water were calculated from the heat, which corresponds to the area of peaks I and II, respectively. On the other hand, the amount of nonfreezing water was obtained as the difference between the combination of free water and freezable bound water and the total amount water in the solution, assuming that the heat of fusion for water is 334 J/g.[3]

Materials

PEG is the most suitable water-soluble polymer with which to investigate the effect of MW, because PEG is inherently a very flexible polymer and has a tendency to show a random-coiled conformation in its aqueous solution.[4] Furthermore, a series of PEGs having different narrow MW distributions are commercially available. PEGs in a variety of MWs (18,000, 10,000, 3500, 2200, 1500, 1000, and 500) were supplied by Sanyo Kasei Kogyo Co. Ltd. (Japan) with the MW data and were used in this study. The MW distribution for each sample was very narrow, and the ratios of weight-average molecular weight (M_w) to number-average molecular weight (M_n) were from 1.01 to 1.07, as shown in Table I. All PEGs were dissolved in deionized water and 5% solutions were prepared for DSC determination. Combinations of two different MW PEGs, except for MW 2200, were also prepared in mixing ratios of 1 : 2, 1 : 1, and 2 : 1.

TABLE I
Average Molecular Weight of the PEG Samples

Sample	M_w	M_n	M_w/M_n
PEG-18000	1.78×10^4	1.76×10^4	1.01
PEG-10000	9.62×10^3	9.37×10^3	1.03
PEG-3500	3.52×10^3	3.45×10^3	1.02
PEG-2200	2.26×10^3	2.19×10^3	1.03
PEG-1500	1.52×10^3	1.46×10^3	1.04
PEG-1000	9.77×10^2	9.24×10^2	1.06
PEG-500	5.37×10^2	5.01×10^2	1.07

RESULTS AND DISCUSSION

Effect of MW of PEG on the dissolved state

The effect of MW on the ratio of free, nonfreezing, and freezable bound waters is shown in Figure 2. The percentage of free water in the solution was nearly constant at about 84% of all water for a MW > 1500 and was a little less than 84% for a MW < 1500.

The percentage of nonfreezing water decreased with an increase of MW up to a MW of 1500 and was nearly constant at about 12% of all water for a MW > 1500. Assuming that the nonfreezing water is the water bound to the polymer molecules uniformly and directly, at least about six water molecules are bound to the repeating unit beyond the MW of 1500. The number of water molecules bound per repeating unit increases to about eight or nine with a decrease in MW, partly because of the end-group effect of the polymer.

The percentage of freezable bound water was negligible up to a MW of about 500 and slowly increased with an increase in MW to a constant value of about 4% of all water for a MW > 2200. Thus, freezable bound water may be detectable at a MW between 500 and 1000. These results suggest that the degree of polymerization (DP) begins to show polymeric characteristics at a value between 11 and 21. The appearance of polymeric characteristics is highly complete at a DP of about 50.

Figure 3(a) shows the effect of MW on peak temperatures for free water and for freezable bound water, which is considered to be the water enclosed by the coiled molecules. Although the peak temperature for free water did not change with MW, the peak temperature for freezable bound water rose with an increase
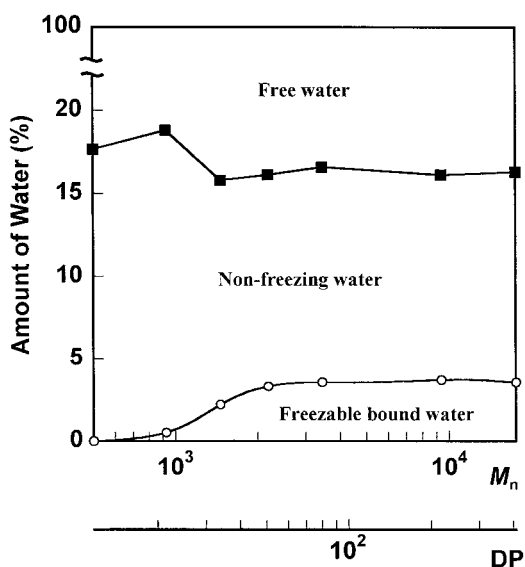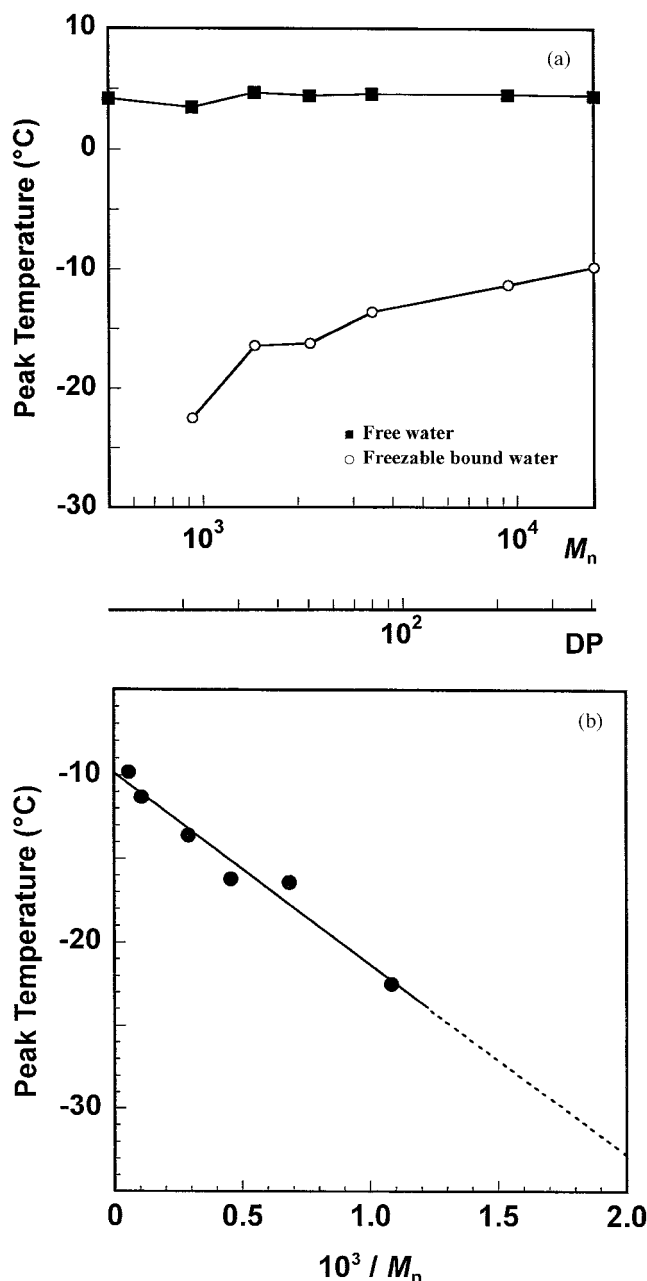

Figure 3 (a) Effect of MW of PEG on the peak temperatures of the DSC curve for free water and freezable bound water. (b) Relationship between the peak temperature for freezable bound water and reciprocal of M_n.

Figure 2 Effect of MW of PEG on the percentage of free, freezable bound, and nonfreezing waters in the solution.

in MW. The increase in the peak temperature in the low MW range was significant. The rise of the peak temperature with an increase in MW might correspond to an increase in the size of the entangled molecular coils in the solution. The relationship between the peak temperature and the reciprocal of M_n is shown in Figure 3(b). A linear relationship suggests that the lowering of the peak temperature with a decrease in MW may be caused by melting point depression.
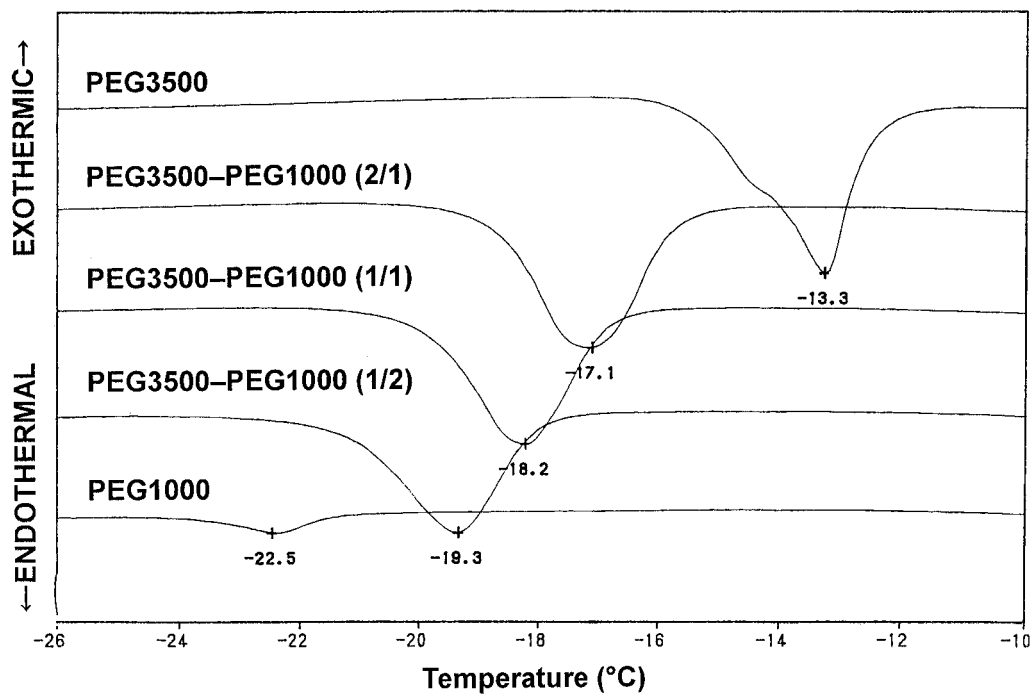
(a)
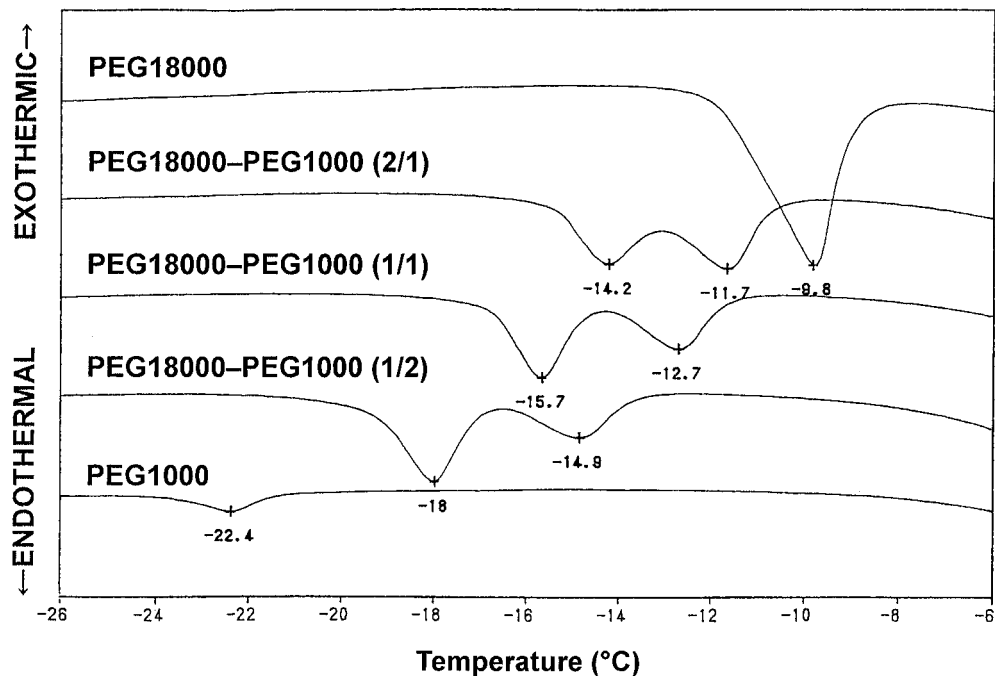
(b)

Figure 4 Heating DSC curves of aqueous solutions of PEG mixed with two different MWs in various ratios. (a) PEG-3500 : PEG-1000 (peak amalgamation type); (b) PEG-18,000 : PEG-1000 (peak separation type).

Effect of mixing two PEGs with different MW on the dissolved state

Classification of mixing into two types

Because the peak temperature for freezable bound water correlated with MW, DSC was expected to be a useful method for measuring the MW distribution.[5] Therefore, two PEGs with different MWs were mixed in a variety of mixing ratios and the resulting DSC curves were examined. The mixing of two PEGs was classified into two types from the shape of the resulting DSC curves for freezable bound water, both the peak amalgamation

TABLE II
Effect of MW Combination on the Classification of Peak Amalgamation or Separation Type[a]

	PEG-1000 (−22.5°C)			
PEG-1500 (−16.4°C)	Amal. 6.1	PEG-1500 (−16.4°C)		
PEG-3500 (−13.6°C)	Amal. 8.9	Amal. 2.8	PEG-3500 (−13.6°C)	
PEG-10000 (−11.3°C)	Sep. 11.2	Amal. 5.1	Amal. 2.3	PEG-10000 (−11.3°C)
PEG-18000 (−9.8°C)	Sep. 12.7	Amal. 6.6	Amal. 3.8	Amal. 1.5

[a] Amal, amalgamation type; Sep, separation type. Values in parentheses show the peak temperature of the DSC curve for freezable bound water. Values beside the peak type for mixtures show the difference between the two peak temperatures of the DSC curve for freezable bound water.

type and the peak separation type, regardless of the mixing ratio. Figure 4(a) and (b) show a series of DSC curves for the freezable bound water at various mixing ratios for the two types of mixing. In the peak amalgamation type [Fig. 4(a)], one peak appeared in the DSC curve at a temperature that was between the temperatures of the two original peaks. On the other hand, two separate peaks appeared in the DSC curve in the peak separation type [Fig. 4(b)]. In both cases the peak temperatures were different from the original peak temperatures. These results suggest that mixing two PEGs with different values for the MW causes a sort of interaction between the two PEGs. The interaction affects the size of the entangled molecular coils (i.e., domains). Therefore, the MW distribution cannot be measured by DSC. The change in size of the entangled molecular coil with the mixing, which is indicated by the change of the peak temperature, could manifest a kind of polymer–polymer interaction. Table II shows the effect of combining two PEGs on the type of DSC curve and the temperature difference between the original two peak temperatures. The original peak temperatures are included for reference.

Generally speaking, the peak separation type was observed when the MW difference was large. The difference in the original molecular sizes of the two polymers, shown as the difference between the temperatures of the original peaks, may be the critical factor that determines whether the peak amalgamation or the peak separation type will result. A temperature difference of about 10°C seems to represent the boundary between the two types.

Effect of mixing ratio on the dissolved state

For the study of the polymer–polymer interaction in the dissolved state, the percentage of freezable water was first examined. Examples of the effect of the mixing ratio of two PEGs that differ in MW on the percentage of free, nonfreezing, and freezable bound waters in the solution are shown in Figure 5(a) for the peak amalgamation type and in Figure 5(b) for the peak separation type. In both examples the lower MW was 1000 and the percentage of freezable bound water increased as more of the higher-MW polymer was added. In both types, the percentage of nonfreezing
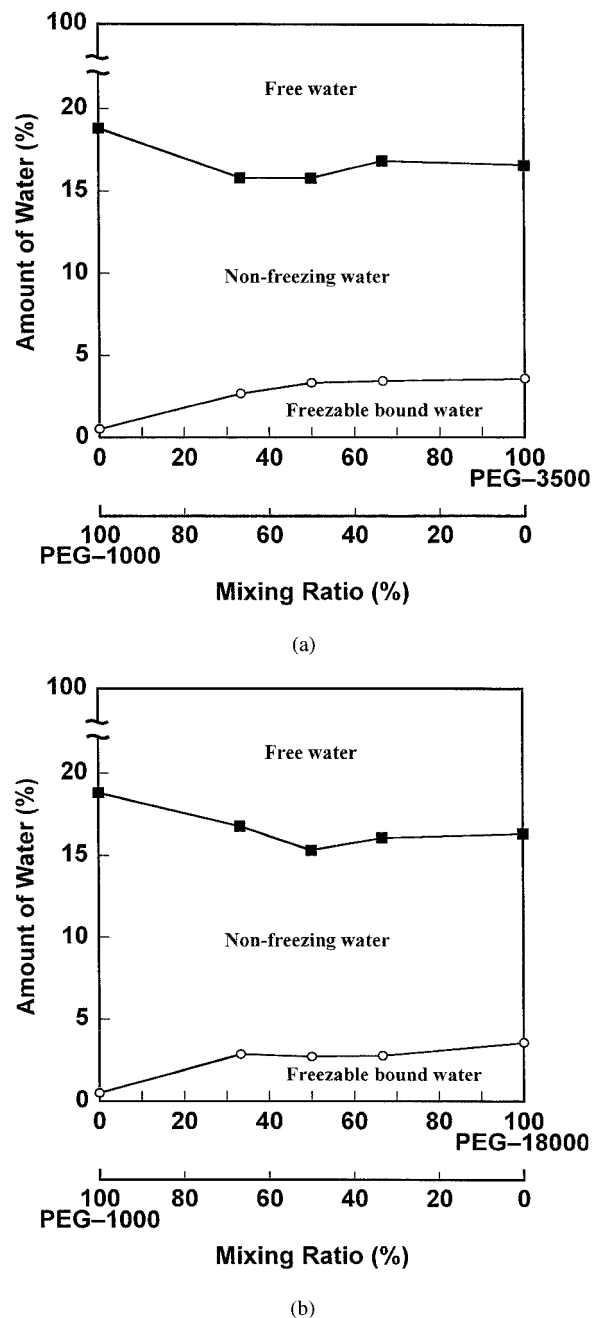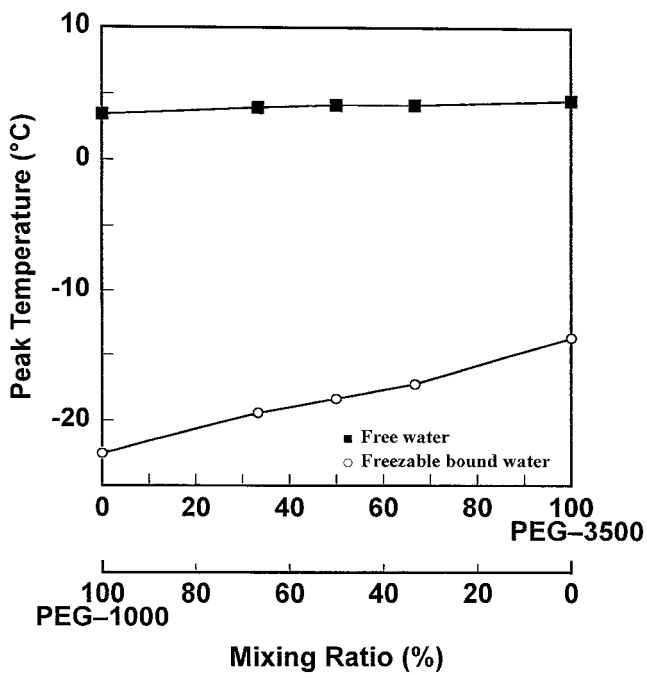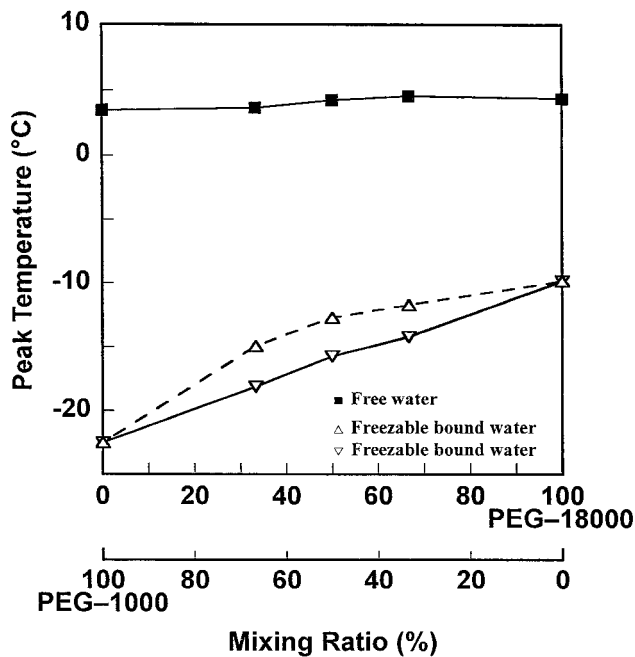

Figure 5 Effect of mixing ratio of two PEGs with different MWs on the percentage of free, freezable bound, and nonfreezing waters in the solution. (a) MWs of 3500 and 1000 (peak amalgamation type); (b) MWs of 18,000 and 1000 (peak separation type).

water initially decreased and, on the contrary, freez-able bound water initially increased with the addition of the higher MW. Further addition of the higher-MW polymer caused almost no change in the percentage of nonfreezing water and little increase in the percentage

(a)

(b)

Figure 6 Effect of mixing ratio of two PEGs with different MWs on the peak temperatures of DSC curves for free water and freezable bound water. (a) MWs of 3500 and 1000 (peak amalgamation type); (b) MWs of 18,000 and 1000 (peak separation type).
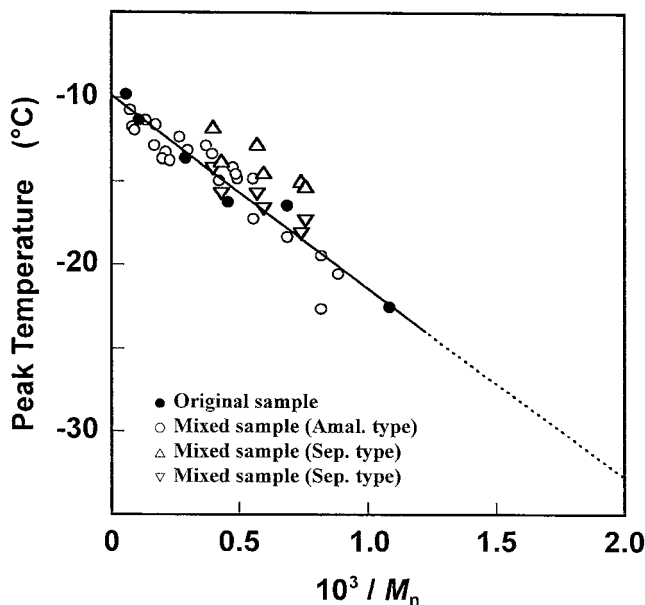

Figure 7 Relationship between the peak temperature for freezable bound water and reciprocal of number-average MW of original PEG and PEG mixtures, including peak amalgamation type and peak separation type.

of freezable bound water. Assuming that freezable bound water is the water enclosed by entangled molecular coils, these results suggest that the addition of a small amount of fully entangled molecular coils may strengthen the entanglement of the molecular coil of the lower-MW polymer.

Peak temperatures as an index of the size of the entangled molecular coils were also examined to investigate the polymer–polymer interaction. Figure 6 shows examples of the effect of mixing ratio of two PEGs that differ in MW on the peak temperatures for freezable bound water and for free water. The MW combinations in Figure 6(a) and (b) correspond to those in Figure 5(a) and (b), respectively. For the peak amalgamation type, the peak temperature was approximately proportional to the mixing ratio. Thus, if the sizes of the entangled molecular coils were not greatly different from each other, the mixing of two MWs converted the two original molecular coils into a single coil of a size nearly proportional to the mixing ratio. On the other hand, for the peak separation type, the peak temperature for higher-MW polymer decreased and that for lower-MW polymer increased with an increase in mixing ratio. Although the change of peak temperatures was roughly proportional to the mixing ratio, the difference between the two peak temperatures seems to increase with an increase in ratio of lower-MW polymer. These results suggest that mixing of the two MWs makes the sizes of the original molecular coils approach each other if the sizes of the original molecular coils are very far apart. The extent of approach was greater with an increase in the proportion of the higher-MW polymer.

TABLE III
Effect of Mixing Ratio of MW 500 and the Higher MW on the Classification of Peak Amalgamation
or Peak Separation Type

PEG-X PEG-X/PEG-500	PEG-1000	PEG-1500	PEG-3500	PEG-10000	PEG-18000
1/0 (only PEG-X)	1 peak −22.5°C	1 peak −16.4°C	1 peak −13.6°C	1 peak −11.3°C	1 peak −9.8°C
2/1	No peak	Amal.	Amal.	Sep.	Sep.
1/1	No peak	No peak	Amal.	Sep.	Sep.
1/2	No peak	No peak	No peak	Amal.	Amal.
0/1 (only PEG-500)			No peak		

The relationship between the peak temperature and the reciprocal of the number-average MW of the original PEG and all PEG mixtures is shown in Figure 7. All PEG mixtures, including both peak amalgamation and separation types, nearly overlap on the linear relationship obtained for the original PEG, except for the high-temperature region of the peak separation type. The linear relationship supports melting point depression as a reasonable mechanism for the peak temperature lowering with a decrease in MW.

**Effect of mixing with very low MW on the dissolved state**

As described above the freezable bound water does not exist in the aqueous solution of PEG with a MW of 500 (PEG-500). If PEG-500 was mixed with other PEG with higher MWs, however, the DSC curve of the mixed solution showed no peak or one peak or two peaks for freezable bond water, depending on the mixing ratio and the MW of the higher-MW polymer. Thus, entanglement of the molecular coil can be developed by the polymer–polymer interaction even with a MW of 500. The effects of MW combination and the mixing ratio on the classification of peak amalgamation or peak separation type for a polymer with a MW of 500 are shown in Table III. When mixed with a MW of 1000 the peak for freezable bound water was not detected regardless of the mixing ratio, although a peak was detected in the solution of only PEG-1000. Furthermore, the peak for freezable bound water was not detected for the combination with PEG-1500 at mixing ratios of 1/1 and 1/2 (PEG-1500/PEG-500) or for the combination with PEG-3500 at a mixing ratio of 1/2 (PEG-3500/PEG-500). Thus, if mixed with a relatively low MW such as 1000, where molecular coil entanglement was not fully developed, and further if the proportion of lower-MW polymer was high, the higher-MW polymer lost its molecular coil entanglement to form a domain dominated by the polymer–polymer interaction with the lower-MW polymer.

When mixed with a MW of 1500 a tiny amalgamated peak appeared at the mixing ratio of 2/1 (PEG-1500/PEG-500). Furthermore, a small amalgamated

peak was detected for the combination with a high MW such as 18,000 at the mixing ratio of 1/2 (PEG-18,000/PEG-500).

When mixed with a MW of 10,000 or 18,000 two small separate peaks for freezable bound water appeared at the mixing ratio of 1/1 and 2/1 (PEG-10,000 or 18,000/PEG-500). The amount of bound water (i.e., the water enclosed by the molecular coils) proportionally decreased with an increase of the ratio of MW 500. Furthermore, an amalgamated peak with a wide shoulder, an intermediate type between the peak amalgamation and peak separation types, appeared at the mixing ratio of 2/1 (PEG-3500/PEG-500). The decrease and disappearance of freezable bound water by the combination with a MW of 500 brought about an increase in the amount of nonfreezing water, which is the water directly bound to the molecules.

Peak temperatures for freezable bound water, as an index of size of the entangled molecular coils, were also examined to clarify more precisely the polymer–polymer interaction for MW 500. Figure 8 shows the effect of the mixing ratio for combinations of MW 500 and higher-MW polymers on the peak temperatures for the peak amalgamation and peak separation types. For the peak amalgamation type the peak temperature proportionally decreased with an increase in MW 500. Thus, the mixing with MW 500 causes a decrease in the size of the entangled molecular coils for the higher-MW polymers. Although the hypothetical size of the molecular coils for MW 500 could be calculated using the linear proportional relationship between peak temperature and mixing ratio, the size varied depending on the MW of the other polymer. For the peak separation type the peak temperature attributed to the higher MW decreased and the peak temperature attributed to MW 500 rapidly decreased with an increase in the proportion of MW 500. Assuming the linearity of the relationship between peak temperature for MW 500 and the mixing ratio, the hypothetical peak temperature for MW 500 was about −31°C. This value agrees with that predicted using the linear relationship shown in Figure 3(b) between peak temper-
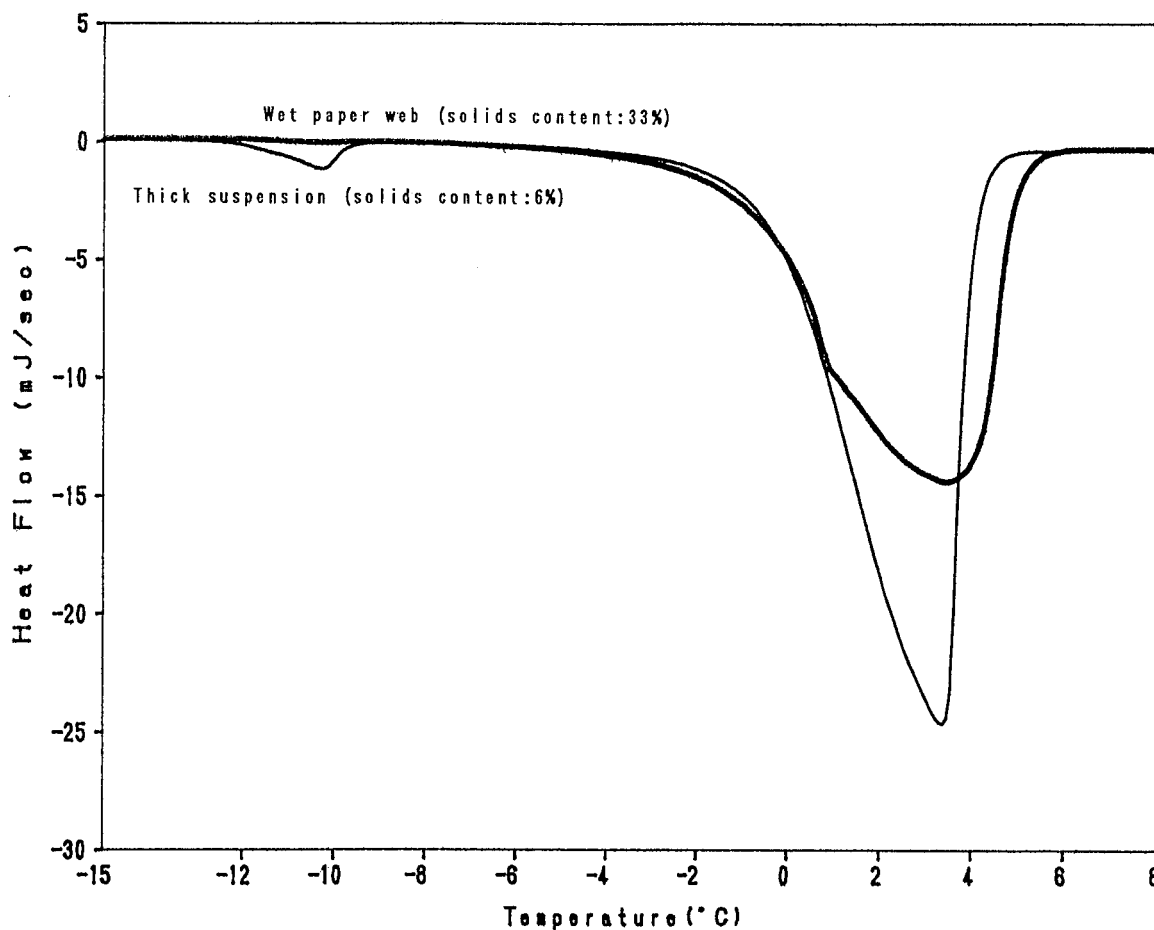
Figure 9 Heating DSC curve of thick suspension of fines-free unbeaten pulp fibers and aqueous 5% PEG (MW: 18,000) solution and that of the wet web from the suspension after wet pressing. Solids contents of the fibers and PEG are 6 and 33%, respectively.

ature and the reciprocal of M_n. These results also show the polymer–polymer interaction as follows. If a molecular coil in which the conformation is not developed (MW 500) is mixed with another molecular coil in which the conformation is not fully developed (MW 1000 or 1500), the higher MW loses or nearly loses its entangled conformation. If a molecular coil in which the conformation is not developed (MW 500) is mixed with another molecular coil in which the conformation is fully developed (MW 10,000 or 18,000), the amount of entangled molecular coils decreases with an increase in the proportion of MW 500. In this case two entangled molecular coils of different sizes appear and both coils are smaller than the original coil of the higher-MW polymer.

CONCLUSIONS

For PEG, the appearance of the characteristics of a polymer in its aqueous solution begins at a DP between 11 and 21 and is largely completed at a DP of about 50. A decrease in the size of the entangled molecular coil with a decrease in MW is indicated by

the lowering of the peak temperature for freezable bound water. Mixing of two MWs in various combinations causes a kind of polymer–polymer interaction. The size of the molecular coil in the mixed-PEG solution generally varies according to a linear relationship between the peak temperature and the reciprocal of the number-average MW. Further studies at various polymer concentrations are expected to clarify more precisely the effect of mixing on the polymer–polymer interaction.

APPENDIX

Effect of web consolidation on the dissolved state

As pointed out in the introduction, the coexistence of polymer and fibers in a paper stock suspension may affect the molecular conformation of the polymer during paper web consolidation. Figure 9 shows the DSC curve
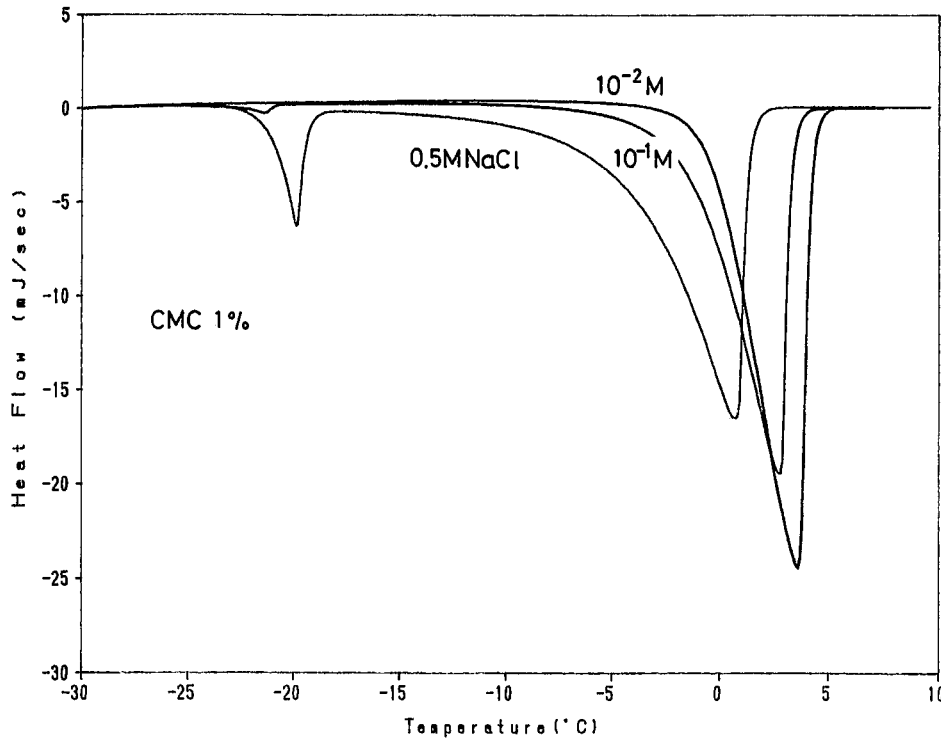
Figure 10 Heating DSC curves of 1% aqueous CMC solutions containing sodium chloride at various levels of concentration.

of a very thick unbeaten kraft pulp fiber suspension in the 5% PEG solution of MW 18,000 (i.e, a mixture of wet pulp fibers and the PEG solution) and the DSC curve of the wet paper web from the suspension. The solids (fi-

Figure 8 Effect of mixing ratio of MW 500 and the higher MW on the peak temperatures of DSC curve for freezable bound water.

bers and PEG) contents are 6% in the thick suspension and 33% in the wet web, respectively. The characteristic peak derived from the water enclosed by the molecular coils at about −10°C was clearly observed in the thick suspension. The space between the pulp fibers in the suspension was full of PEG solution and the peak could have arisen from the PEG solution between the fibers. On the other hand, with a solid (mainly fibers) concentration of 33%, this peak (i.e., the water enclosed by the PEG molecular coils) nearly disappeared. A magnification of the DSC curve was required to detect a tiny peak at about −10°C. As a plausible mechanism for the disappearance, either the displacement of PEG solution between the fibers in favor of air or a change in the molecular conformation of PEG polymer remaining on the surface of the fibers could be considered. Further studies conducted on different pulps beaten to various degrees are required to investigate the relationship between the peak disappearance and the solid concentration.
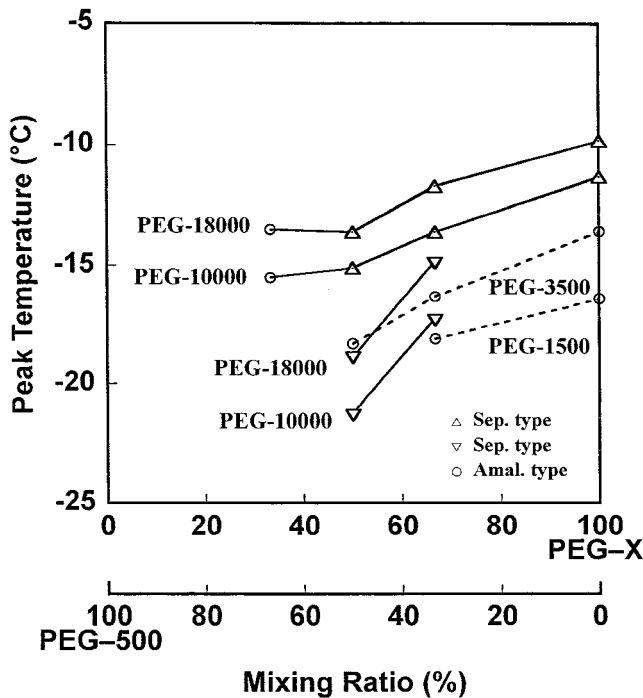
Effect of electrolytes on the dissolved state of a polyelectrolyte

Because a recycle system of water for papermaking has been developed, electrolyte concentration in the water has increased.[6] Many polymers employed for papermaking such as carboxymethylcellulose (CMC) and polyacrylamide (PAM), which are used as dry strength resins, contain electric charges in their molecules (i.e., they are considered as a kind of polyelectrolyte). The

increase in electrolyte concentration may affect the molecular conformation of a polyelectrolyte in the solution. Figure 10 shows the effect of NaCl concentration on the DSC curve of a 1% solution of a commercial CMC. Although no peak for freezable bound water was observed in the most dilute (10^{-2} M) NaCl solution, the peak appeared in a 10^{-1} M solution and increased in size with an increase in NaCl concentration. This means that entanglement of the CMC polymer chain increases with an increase in electrolyte concentration. Thus, electrolyte in the solution neutralized charges in the CMC polymer chain and the conformation changed from extended to entangled as a result.

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