Polymer Aqueous Solutions as Quenching Media. II. Ethylene Oxide–Propylene Oxide Copolymers

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SYNOPSIS

The cooling power of aqueous solutions of ethylene oxide–propylene oxide copolymers are studied with a silver standard sample by using two apparatuses quench with injection and quench with agitation. For temperature T > 400°C, the viscosity plays the predominant role; for T < 400°C, the cooling is controlled by the polymer precipitation and the cooling rate decreases by lowering the cloud point of the polymer solution. This work demonstrates the possibility of adjusting the cooling curves by taking into account the thermodynamical properties of the polymer.

INTRODUCTION

Quenching is the process whereby a metallic work-piece heated to a given elevated temperature is cooled by immersion in a quenchant medium such as water, aqueous solutions, or mineral oils. The cooling rate is dependent on factors such as the size, shape, and nature of the workpiece as well as the composition, velocity, and temperature of the liquid.

For most of the steels, mineral oils are used because of their relatively high convection temperature (θ_2). However, the unavoidable stage of film boiling leads to cooling rates too low in the high temperature range and this constitutes with fire hazard and toxicity the well-known disadvantages of such fluids. It is the reason why substitution media such as polymer quenchants are the object of intensive researchs since 15 years.

In a first step, it has been shown that film boiling is unstable in the case of subcooled liquid (water or aqueous solutions) and its destabilization can be easily controlled by liquid agitation.[1]

We have recently undertaken a systematical study of the influence of concentration and molecular weight on the heat transfer (without film boiling) in the case of polyvinylpyrrolidone.[2] The ob-

served behaviors cannot be simply explained by a viscosity effect but lead to assume that a polymer deposit on the workpiece modifies the heat transfer by acting as thermal resistance.

The case of aqueous solutions where phase separation occurs by heating [case of ethylene oxide–propylene oxide copolymers (EO–PO) solutions] was then particularly interesting to study.

In this paper which deals with the cooling power of these copolymer solutions, we are going to show the dependence of cooling rate on the following:

—polymer concentration
—polymer composition
—nature of additive
—concentration of additive

EXPERIMENTAL

Polymer Samples

The EO–PO copolymer samples have been furnished by Atochem. The copolymer chains have star structure (three branchs).

We have already made detailed characterizations of these copolymers and we have already carried out an extensive study of the thermodynamical properties of their aqueous solutions.[3,4] The determinations of cloud points, T_t, were made with a Mettler apparatus. The viscosity measurements were per-

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Table I   Characteristics of Copolymers Samples

Sample	$M_w \times 10^{-4}$	I	$A_2 \times 10^3$	$[\eta]$ $(cm^3\ g^{-1})$ $(25°C)$	T_t
A $Y = 0.193$	3.25	1.47	1.25	38.60	73.60
B $Y = 0.263$	3.60	1.15	0.60	32.60	66.00
C $Y = 0.194$	3.08	1.18	105	34.30	74.40
D $Y = 0.121$	3.01	1.20	2.15	37.50	86.80

formed with an automatic capillary viscosimeter. In Table I, we give only the most important properties of the samples used in this study:

M_w = weight average molecular weight

A_2 = second virial coefficient at 25°C

                        in pure water

I = polydispersity index

$[\eta]$ = intrinsic viscosity in water at 25°C

                        $(cm^3\ g^{-1})$

T_t = cloud point for $c_p = 4\%$ by weight in water

Quenching Tests

The study was made with different concentrations for every copolymer and every additive. The cooling power of solutions was determined with a silver standard sample by using two apparatuses quench with injection and quench with agitation of the solution. The details of these apparatuses are given in Ref. 2. For injection tests the liquid velocities were 3.0, 5.5, and 9.0 m s^{-1} and the bath temperature was 25°C; as the behaviors were the same in the three cases, we will only consider the results obtained at injection speed of 5.5 m s^{-1}. In the tests with agitation the liquid velocity was 0.4 m s^{-1} and the bath temperature was 30°C.

RESULTS

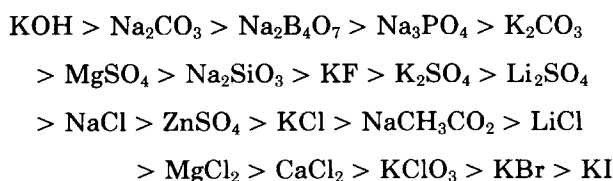### Characterization of the Copolymer Samples

Cloud Point

In Figure 1, we give an example of variation of T_t with polymer concentration. The phase diagram is

identical to that described for PEO[5] [poly(ethylene oxide)]. We have recently shown that T_t decreases with increasing fraction (Y) of PO units[3] according to a linear relation:

$$T_t = 102.5 - 154.5Y \quad (°C) \qquad (1)$$

Addition of salts generally lowers T_t (Fig. 2). The order of the "salting out" effectiveness of the different salts compared at equal molar concentration seems to be nearly the same for our copolymers as for PEO.[4] This order is reminiscent of Hofmeister series for proteins. From the experimental results of Refs. 4, 5, and 6, one can classify these salts at equal weight concentration by decreasing effect as following:

$KOH > Na_2CO_3 > Na_2B_4O_7 > Na_3PO_4 > K_2CO_3$

$> MgSO_4 > Na_2SiO_3 > KF > K_2SO_4 > Li_2SO_4$

$> NaCl > ZnSO_4 > KCl > NaCH_3CO_2 > LiCl$

$> MgCl_2 > CaCl_2 > KClO_3 > KBr > KI$

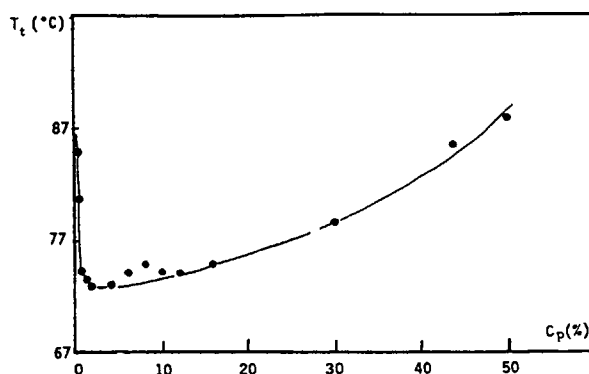Organic additives can have a lowering or an increas-

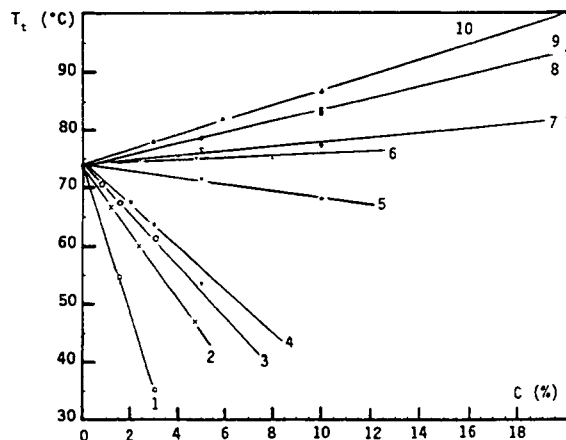**Figure 1**   Demixing curve for sample A in pure water.

Figure 2 Variation of cloud point of the polymer A solution with additive concentration: (1) sodium carbonate; (2) sodium phosphate; (3) borax; (4) n-butanol; (5) n-propanol; (6) potassium iodide; (7) ethylene glycol; (8) ethanol; (9) propylene glycol; (10) acetamide.

Figure 3 Dependence of the cooling curves for sample A solutions on polymer concentration c_p (g L^{-1}): (- - -) pure water; (———) 10; (— —) 20; (— O —) 30; (— △ —) 80.

ing effect on T_t (Fig. 2). These effects are more complex because they probably result from a balance between the enthalpic effect of polymer-additive and water-additive interactions and the entropic effect arising from the change in the water structure in the neighborhood of the hydrophobic part of the additive, both effects depending on the length of hydrocarbon chain, the nature of the polar group, and the isomerism of the additives.[7]

Viscosity

In a previous work,[4] we discuss the variation of intrinsic viscosity [η] with the concentration of different mineral or organic additives.

In Table II, we have reported some results for one additive of each type, Na_2CO_3 and propylene glycol, which we have often used in the present work. They show the effect of these additives on some characteristic parameters of the solution in the case of copolymer A (solvent and solution viscosities η_0 and η respectively, intrinsic viscosity [η], T_t, and pH) at 25°C. We consider the binary mixture, water-additive, as the solvent. η_0 increases with additive concentration but η depends on the nature of additive and reflects its influence on the conformational properties of the polymer: Addition of Na_2CO_3 strongly lowers the hydrodynamical volume of the macromolecule and the resulting [η] decrease dominates the increase of solvent viscosity. In the case of propylene glycol, which has an increasing effect on [η] as well as on η_0, η increases greatly with its concentration.

Quenching Tests

Effect of Polymer Concentration

Figures 3 and 4 show the influence of the polymer concentration on cooling curves and cooling rate curves, respectively, for sample A in a given formulation (tests performed by agitation).

Two important behaviors must be noted:

—When c_p increases, the maximum of the cooling rate decreases and is shifted toward the high temperatures (370°C for pure water and 560°C for solution at 80 g L^{-1}). Such a decrease is in agreement with the findings of Hilder[8] (agi-
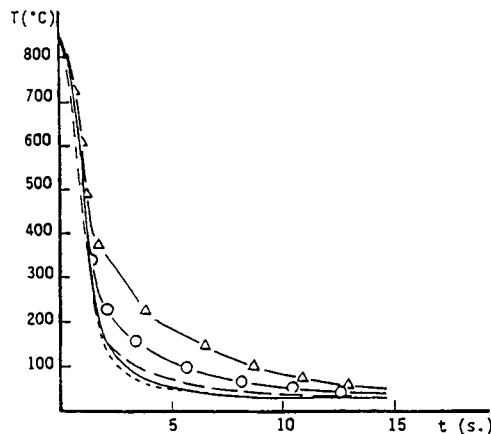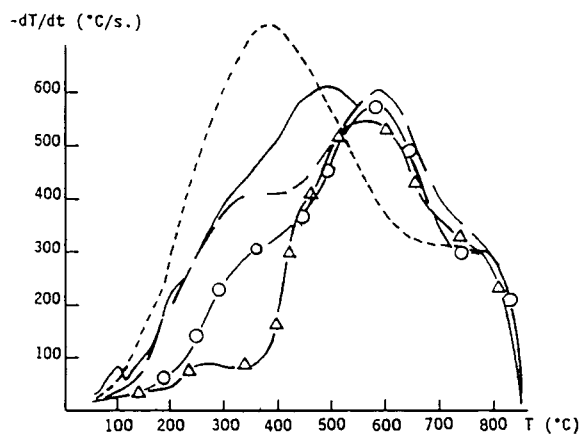

Figure 4 Dependence of the cooling rate curves for sample A solutions on polymer concentration c_p (g L^{-1}): (- - -) pure water; (———) 10; (— —) 20; (— O —) 30; (— △ —) 80.

tation rate was 0.5 m s^{-1}) and Masson and Lake[9] for still PAG [poly(alkylene glycol)] solutions. These last workers have observed a linear decrease of the cooling rate maximum with increasing polymer concentration, whereas our results, in agreement with those of Hilder et al.,[8] show an important deviation from linearity.

—In the range of temperature lower than 550°C the cooling rate decreases with increasing polymer concentration.

These results can be qualitatively understood by distinguishing the stage of nucleate boiling and the stage of forced convection, as already made in the case of polyvinylpyrrolidone solutions.[2]

One may think that, in the first stage, the increase of viscosity hinders the formation of solvent bubbles and their evacuation into the solution. This reduces the length of this stage and the cooling rate. Such a behavior has already been investigated by Moreaux et al.,[10] who have shown that the transition temperature between nucleate boiling and convection (θ_2) is an increasing function of polymer concentration. In fact, there are no predictions for the dependence of cooling rate on polymer concentration or on solution viscosity in this stage and one may assume that other parameters play a role such as the interfacial tension.

In the second stage, which could be considered as that of convection, the empirical laws of heat transfer allow us to think that the driving parameter is also the solution viscosity. However, the depen-
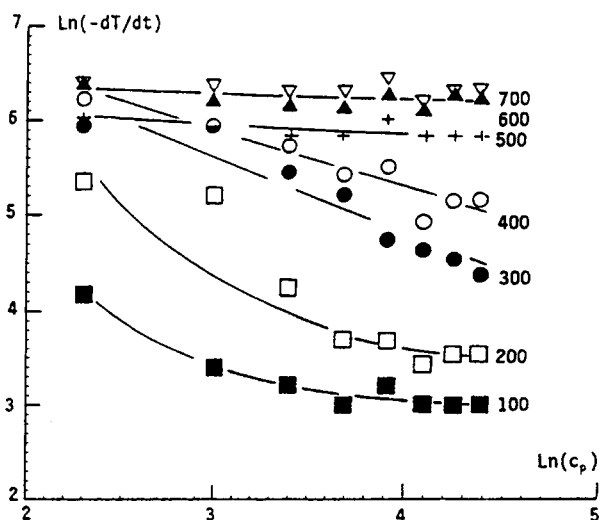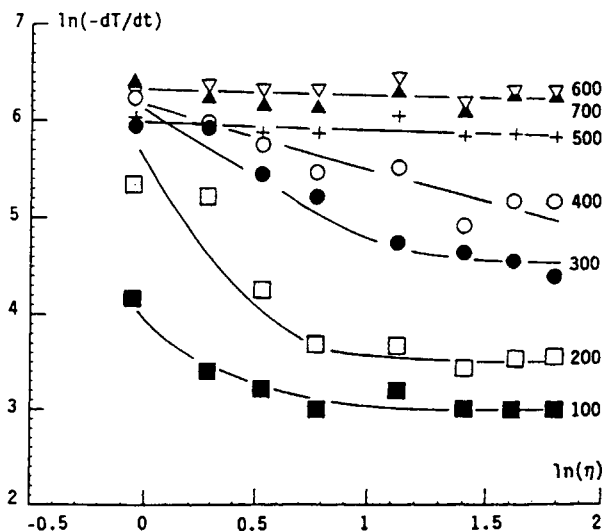

Figure 6 Logarithmic plot of cooling rate versus solution viscosity ($\eta_{40°C}$) at different temperatures.

dence of the Nusselt number expected in the case of a laminar flow in the direction of the axis of a cylinder is: ν proportional to $\eta^{-1/6}$. This prediction was not verified in our previous experiments carried out with polyvinylpyrrolidone solutions and a much higher absolute value of this exponent has been obtained.[2] We have attributed these discrepancies to the formation of a polymer deposit acting as a thermal resistance and perturbing the heat transfer, which becomes slower than in the case of water.

The same arguments can be used to discuss the results of this paper, by assuming that the thermodynamical properties of EO–PO copolymer solutions enhance the effect of thermal resistance of the polymer deposit. More precisely, in the case of PVP, one can consider that the polymer deposit is only due to the dehydration, which occurs during boiling while, in the present case, the thermodynamical demixing at high temperature plays the main role in the formation of the polymer deposit.

From this point of view and in order to establish simple relations between the polymer concentration (c_p) or the solution viscosity at 40°C (η) and the cooling rate, we have plotted in logarithmic scales the cooling rate versus c_p (Fig. 5) and versus η (Fig. 6) at different temperatures. It can be seen that the logarithm of cooling rate depends slightly on c_p and η for temperatures > 500°C.

For temperatures < 400°C, there is a decrease of the rate up to $c_P = 38$ g L^{-1} or $\eta_{40} = 2$ mPa s and after the cooling rate becomes independent on polymer concentration. In the case of PVP solutions we have not observed such behavior change since the

Figure 5 Logarithmic plot of cooling rate versus polymer concentration (sample A) at different temperatures.

logarithmic plots of cooling rate versus c_P and η remain quite linear in the whole explored range of concentration.[2] Bozhko et al.[11] have suggested the existence of a critical viscosity (solutions containing a nonionic polymer called PPS) above which the cooling rate tends to level off. This result is particularly interesting for two reasons:

—From a practical point of view, it indicates the maximum of concentration, allowing us to obtain the best efficiency of the cooling process.

—On the other hand, it is interesting to compare the curves of cooling rate versus c_P of Figure 5 with the binodal curve of Figure 1. One can see that the cloud point T_t decreases with c_P up to 3% approximately and does not much vary for c_P ranging between 3 and 6%. The cooling rate seems to follow the same variation and there is probably a correlation between the value of the cloud point of the solutions and the cooling rate in the stage of convection. One may assume that the efficiency of the deposit of a concentrated polymer phase in reducing the cooling rate depends on its "lifetime" and its concentration, which will determine its thermal resistance power. The first parameter is directly related to the value of the cloud point since the lower the cloud point, the faster its formation and the slower its redissolution. The concentration of the deposit can be deduced from the binodal curves[3] and it is obvious in Figure 1 that it increases by increasing the difference ΔT between temperature and the lower critical solution temperature (LCST') corresponding to the minimum of the binodal curve. At the same ΔT the volume fraction of the concentrated polymer phase is proportional to concentration and this last effect partially explains the high dependence of cooling rate on c_P up to 38 g L^{-1}. All these arguments support the idea of using the cloud point of the solution as a good parameter to study the effect of the demixing on the cooling rate in the stage of convection at least in a first approximation. The purpose of our following investigations was to verify such an hypothesis by studying systems having different cloud points.

Effect of Copolymer Composition

In Figure 7 we compare the cooling power of solutions of samples B and D in pure water at the same concentration (40 g L^{-1}). One can note that in the range of temperatures below 400°C, the polymer B solution of lowest T_t (see Table I) corresponds to the lowest cooling rate, in agreement with our assumptions. In the range of high temperatures, the little difference in cooling curves can be due to the
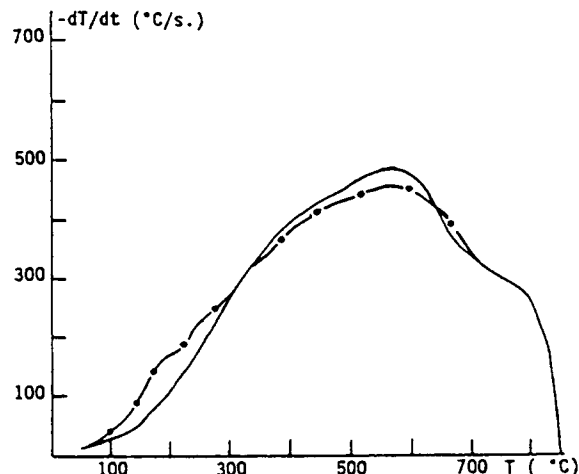

Figure 7   Cooling rate curves obtained by agitation for samples B (———) and D (— ● —).

slight difference of solution viscosities ($\eta_B = 1.81$ and $\eta_D = 1.95$ mPa s at 40°C for B and D, respectively). The less viscous solution (B) less hinders the formation of solvent bubbles.

Effect of Additives

Moreaux et al.[10] have shown the dependence of θ_2 (temperature of transition nucleate boiling–convection) on the nature and the concentration of additives. In this work we make their preliminary results precise by using other additives and investigating the cooling rate evolution in the whole temperature range. These tests were made by injection. We have essentially studied the influence of additives on cooling power of sample A solutions.

Figure 8 gives some examples of cooling curves obtained by addition of organic compounds and mineral salts on a solution of polymer A at 40 g L^{-1}. These results must be discussed by considering the lowering and increasing effects of the additives on the cloud point (see Fig. 2). Figure 8 illustrates well the existence of two different domains of temperature:

$$T > 400°C: \text{domain } \mathbf{A}$$

$$T < 400°C: \text{domain } \mathbf{B}$$

since all curves intersect near this temperature. Such a temperature value is close to the transition between the two cooling stages.

The (three) sodium phosphate which lowers T_t tends to reduce cooling rate in the domain **B** while in the domain **A** it tends to accelerate the cooling. This second behavior can be explained by the de-
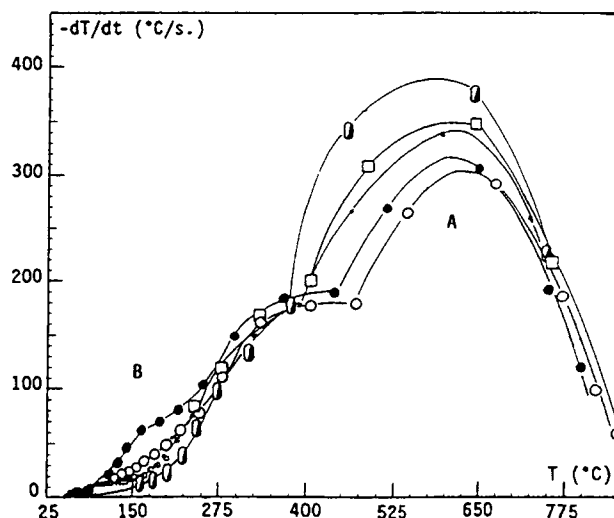
Figure 8   Variation of the cooling rate with the nature of the additives: sample A in pure water ($\square$), with sodium phosphate at 4% ($\mathbf{\Phi}$), potassium iodide at 4% ($*$), acetamide at 10% ($\bullet$), and ethylene glycol at 10% ($\bigcirc$).

crease of the solution viscosity, allowing the formation of solvent bubbles and enhancing heat transfer. (Sodium phosphate has the same lowering effect on viscosity as sodium carbonate; see Table II and Ref. 4).

The addition of potassium iodide which has a little effect on both cloud point and viscosity (see Fig. 2) does not change the cooling rate curve with respect to that of pure water.

As expected from the cloud point variations, acetamide and ethylene glycol give an effect opposite of that observed with sodium phosphate. These additives increase the cloud point (see Fig. 2) and the solution viscosity. They facilitate the polymer redissolution and induce a weakness of the effect of thermal resistance constituted by the polymer de-
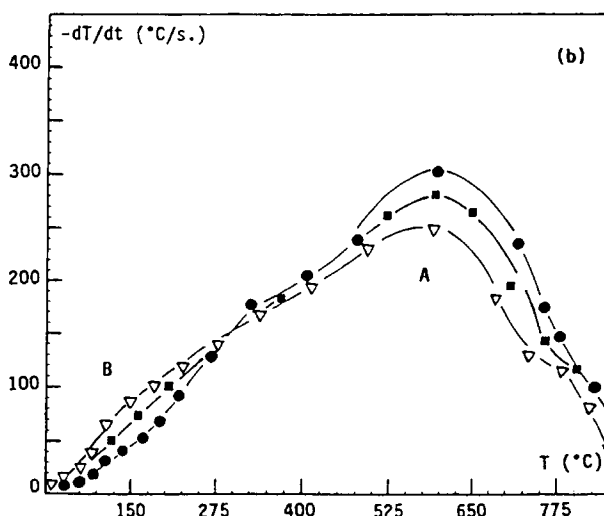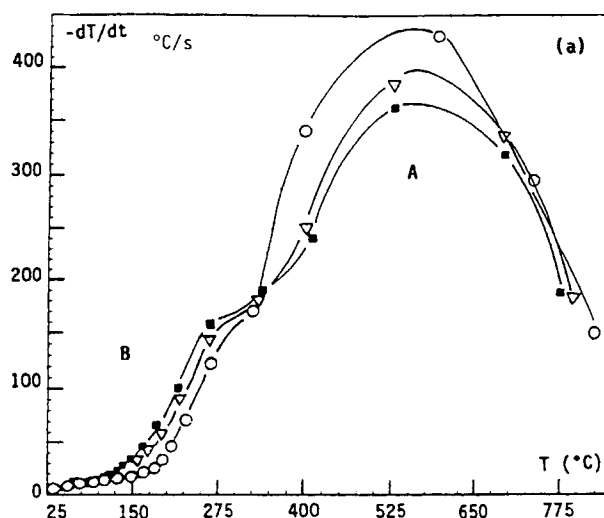

Figure 9   Variation of the cooling rate: (a) With Na_2CO_3 concentration (%): ($\blacksquare$) 0.76; (∇) 1.52; ($\bigcirc$) 3.04: (b) With propyleneglycol concentration (%): ($\bullet$) 5; ($\blacksquare$) 10; (∇) 20.

Table II   Effect of Additives Concentration on Some Solution Properties of Copolymer A[a]

	Additives					
	Na_2CO_3				Propylene Glycol	
C_A (%)	0	0.76	1.52	3.04	5	10	20
η_0 (mPa s)	1	1.03	1.06	1.13	1.2	1.4	1.8
η (mPa s)	3.5	3.40	3.27	3.01	4.14	4.72	5.90
$[\eta]$ (cm^3 g^{-1})	38.6	—	—	29.70	—	—	43.80
T_t (°C)	73.6	64.4	54.8	35.3	78.6	83.5	96.0
pH	7.9	—	—	11.50	—	—	6.9

[a] η, T_t, pH are given for a polymer concentration c_p = 4% (g/g).

posit around the workpiece. Then an increase of cooling rate is observed in the convection stage (domain **B**). They also induce a cooling rate decrease and a shift of its maximum in the domain **A**, where the viscosity effects are predominant.

We have studied the effect of the concentration of additive in the cases of Na_2CO_3 and propylene glycol, which have important and opposite influence on cloud point and viscosity (see Fig. 2 and Table II). In Figures 9(a) and 9(b), we find again the same domains **A** and **B**.

    —In the domain **A**, the cooling rate at a given temperature increases by addition of sodium carbonate and decreases by addition of propylene glycol.

    —In the domain **B**, the opposite effects are observed.

The results dealing with the effects of additives confirm without any ambiguity the existence of two distinct temperature domains and we can make the behaviors precise in each of these domains as follows:

It is generally expected that cooling process is slower when the viscosity of the quenchant increases without taking into account demixing phenomenon. In general, if the additive is organic, the solution viscosity increases; if the additive is mineral, the solution viscosity decreases. In Figure 10, we have gathered the rate values measured at different tem-
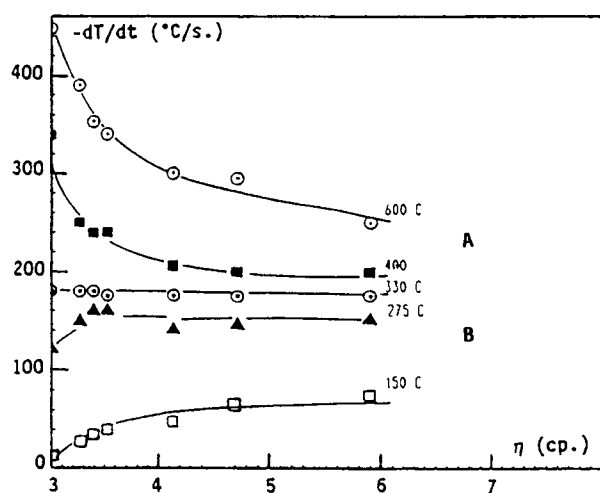

Figure 11   Cooling rate measured at different temperature versus cloud point of the solution for sample A (same note as for Fig. 10).

peratures versus solution viscosity in the case of addition of sodium carbonate and propylene glycol. It clearly appears that in the domain **A** the expected behavior is obtained while in the domain **B** the cooling rate becomes an increasing function of the viscosity. This is additional proof that the viscosity is not the driving parameter any more in the low temperature range, where the demixing plays the predominant role. In Figure 11, we have plotted cooling

Figure 10   Cooling rate measured at different temperatures versus viscosity for sample A. Note: The three first points are obtained for addition of Na_2CO_3, the fourth one corresponds to sample A in pure water and the last points are obtained for addition of propylene glycol.
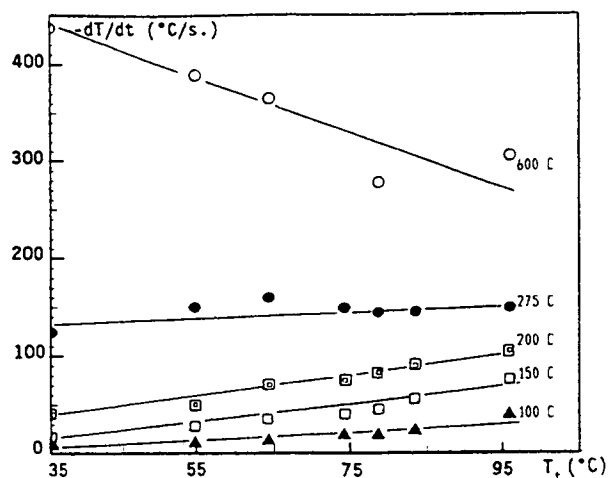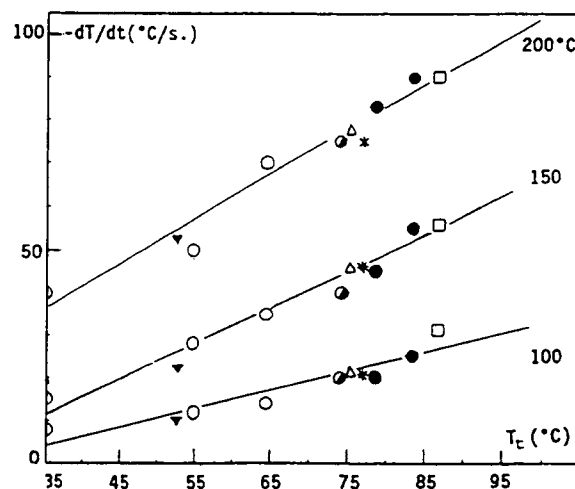

Figure 12   Cooling rate measured at different temperatures for sample A versus cloud point with different additives at different concentrations: (O) Na_2CO_3; (▼) sodium phosphate; (◐) poplymer alone; (△) potassium iodide; (*) ethylene glycol; (●) propylene glycol; (□) acetamide.

rates as a function of cloud points. The cooling rate is a linear function of cloud point in the domain **B**. This is generalized in Figure 12, where we have reported in the same representation the cooling rates obtained with all the additives.

CONCLUSION

In this work, we have studied the dependence of cooling rate on different parameters for a class of polymers able to present demixing by heating: composition and concentration of the polymer, nature, and concentration of the additives.

We conclude that two temperature domains exist: In the range of high temperatures (nucleate boiling), the observed behaviors can be classically attributed to viscosity effects. In the range of low temperature (convection stage), the existence of a lower critical solution temperature induces the precipitation of the polymer, which greatly influences the cooling rate. This result is very interesting because it demonstrates the possibility of adjusting the cooling rate curve on the simple basis of the thermodynamical properties of the polymer and from a cloud point measurement.

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