Phase-Separation Phenomena in the Polymerization of Styrene in the Presence of Polyethylene Wax

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ABSTRACT: The demixing processes that occur during the polymerization of styrene in the presence of a low molar mass polyethylene wax were investigated. Quantitative information on the phase behavior of such a three-component system was obtained through the investigation of the temperature-induced phase separation and the observation of the phase separation during polymerization. Both techniques allow the construction of the same ternary phase diagram. Such phase behavior can be understood through the discussion of the interference of a liquid–liquid phase-separation process and crystallization. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2234–2243, 2004

Key words: polystyrene; polyethylene wax; phase separation, phase diagrams; additives

INTRODUCTION

Polymerizations are often carried out in the presence of additives, dissolved in the reaction medium, consisting of low molar mass substances as well as polymers with a chemical structure different from that of the polymerizing system.[1–5] During such polymerization phase-separation processes can occur. This involves liquid–solid (L-S) phase separation or crystallization, as well as liquid–liquid (L-L) phase separation. A well-defined morphology can result because the additive will be dispersed as a separated phase through the polymerized matrix. The following aspects should be taken into account:

- L-S phase separation or crystallization will lead to the formation of a dispersion of crystals. The final morphology will be "frozen" when the system is cooled below its glass-transition temperature of this polymerized matrix.
- L-L phase separation will lead to two solutions of different composition in equilibrium with each other. This can result in a dispersion of droplets of one solution in the matrix of the second solution. As long as this system remains in the liquid, polymerizing state, such droplets can ripen by coalescence. This will, of course, be influenced by the viscosity and therefore by the temperature of polymerization, the degree of conversion that depends on the time of polymerization, and the molar mass of the polymer that is formed. The morphology is fixed only when the system is cooled to a temperature below the glass-transition temperature of the polymerized matrix.

- Interference of both phase transitions can lead to materials with interesting morphologies and properties. Such a situation is encountered in the radical polymerization of vinyl monomers in the presence of a hydrocarbon polymer like polyethylene, dissolved in the polymerizing monomer.[6,7]

To control the properties of the resulting material, a fundamental insight into the different processes that occur during the polymerization is needed. The exact nature of the demixing processes and their mutual interference has to be investigated. An interesting situation is encountered when L-L demixing precedes crystallization in the concentration domain of interest.[8–12]

A typical example of such a polymerization process is the radical polymerization of styrene in the presence of small quantities of a low molar mass polyethylene wax (PEW), dissolved in the polymerizing solution. The purpose of this article is to approach this problem by investigating the demixing processes mainly through thermally induced phase separation (TIPS) in solutions containing the three components: atactic polystyrene (PST), PEW, and styrene monomer (ST). Such experiments must be performed in the presence of the necessary amount of stabilizer to avoid polymerization during the experimental observations. Some aspects of the demixing processes will also be approached through polymerization experiments that

TABLE I
Molecular Characteristics of PEW

Molecular characterstics	PEW1	PEW2	PEW3
$\bar{M}_w$ [g/mol]	6.8×10^3	7×10^3	0.81×10^3
$\bar{M}_n$ [g/mol]	1.6×10^3	3.1×10^3	0.5×10^3
$\bar{M}_w/\bar{M}_n$	4.3	2.3	1.6
$CH_3/1000C$	26.1	12	1.1

start from a solution of PEW in ST. This will be called polymerization-induced phase separation (PIPS).

EXPERIMENTAL

Materials

Styrene was supplied by Shell and used as received without any further purification.

The polyethylene waxes were also supplied by Shell. The molecular characteristics (number- and mass-average molar masses $\bar{M}_n$ and $\bar{M}_w$, respectively), their ratio ($\bar{M}_w/\bar{M}_n$), and the number of CH_3 branches per 1000 carbon atoms ($CH_3/1000C$) are reported in Table I.

Styrene (ST), used for the TIPS investigations, was stabilized by a combination of 2,2,6,6-tetramethylpiperidino-oxy (Janssen Chimica) and p-benzoquinone (Acros Organics). Polystyrene (PST) was supplied by Shell. The average molar masses are $\bar{M}_w = 178 \times 10^3$ and $\bar{M}_n = 66 \times 10^3$ g/mol.

Dibenzoyl peroxide, in the presence of nitroxyl radical, was used as the initiator for the polymerization.

Concentrations are expressed in weight fractions w_i, where i represents the dissolved component.

Investigation of the phase-separation processes

TIPS

Two techniques were used: calorimetry and cloud point (CP) measurements.

The calorimetric experiments were performed with the DSC7 Perkin–Elmer (Perkin Elmer Cetus Instruments, Norwalk, CT). The samples were preheated at 130°C and homogenized for 10 min in the DSC cell. Then the cooling and heating scans were recorded at the scanning rate of 2°C/min.

Cloud point (CP) measurements were performed by turbidimetry. The ST/PEW solution was homogenized at 140°C and then cooled at 2°C/min. The temperature at the onset of the decrease of the intensity of the transmitted light was taken as the CP.

Miscibility of PEW–styrene–PST

Solutions of PST in stabilized ST were prepared. Different amounts of PEW were added to these solutions in glass tubes sealed under vacuum, and were homog-

enized at 140°C. The transparent solutions obtained in this way were cooled at 2°C/min and their CPs were recorded by turbidimetry. Because of the limited solubility of PEW in the system ST/PST, only samples with rather low PEW content ($w_{PEW} \leq 0.10$) could be investigated.

PIPS

During isothermal polymerization of styrene in the presence of PEW, the phase-separation process is induced by the transformation of ST into PST. The correlation between the onset of this phase separation and the degree of conversion during the polymerization was studied through the combination of dilatometry (degree of conversion as a function of time) and CP determination.

The reaction vessel of the dilatometer was filled with PEW and monomer in which 0.01 mol of dibenzoylperoxide and 6.25×10^{-4} mol of nitroxyl radical were dissolved. The inhibitor was used to control the starting point of the styrene polymerization.

The dilatometer was immersed into a water bath whose temperature was controlled with an accuracy of ±0.1°C. The measurements were performed at 90°C. The volume contraction during polymerization is a direct measure of the increase of the degree of polymerization as a function of time. The degree of conversion (x) was calculated from the change of the height of the mercury column in the dilatometer:

$$X(\%) = K \frac{\Delta V}{V_0} \times 100$$

where ΔV is the volume change, V_0 is the initial volume, and K is the contraction factor. This factor is related to the specific volumes of the monomer ($\tilde{V}_{mon}$) and the polymer ($\tilde{V}_{pol}$):

$$K = \frac{\tilde{V}_{mon}}{\tilde{V}_{mon} - \tilde{V}_{pol}}$$

The value of $K = 5.59$ for styrene at 90°C was used.

RESULTS AND DISCUSSION

Characteristics of PEW

Dynamic observations

The waxes chosen for these experiments differ by their molar mass, molar mass distribution, and degree of branching. Their crystallization and melting behaviors were studied by DSC and the corresponding scans are represented in Figure 1. The melting points (T_m), reported in Table II, correspond to the temperature at the end of the melting endotherm. The crystallization
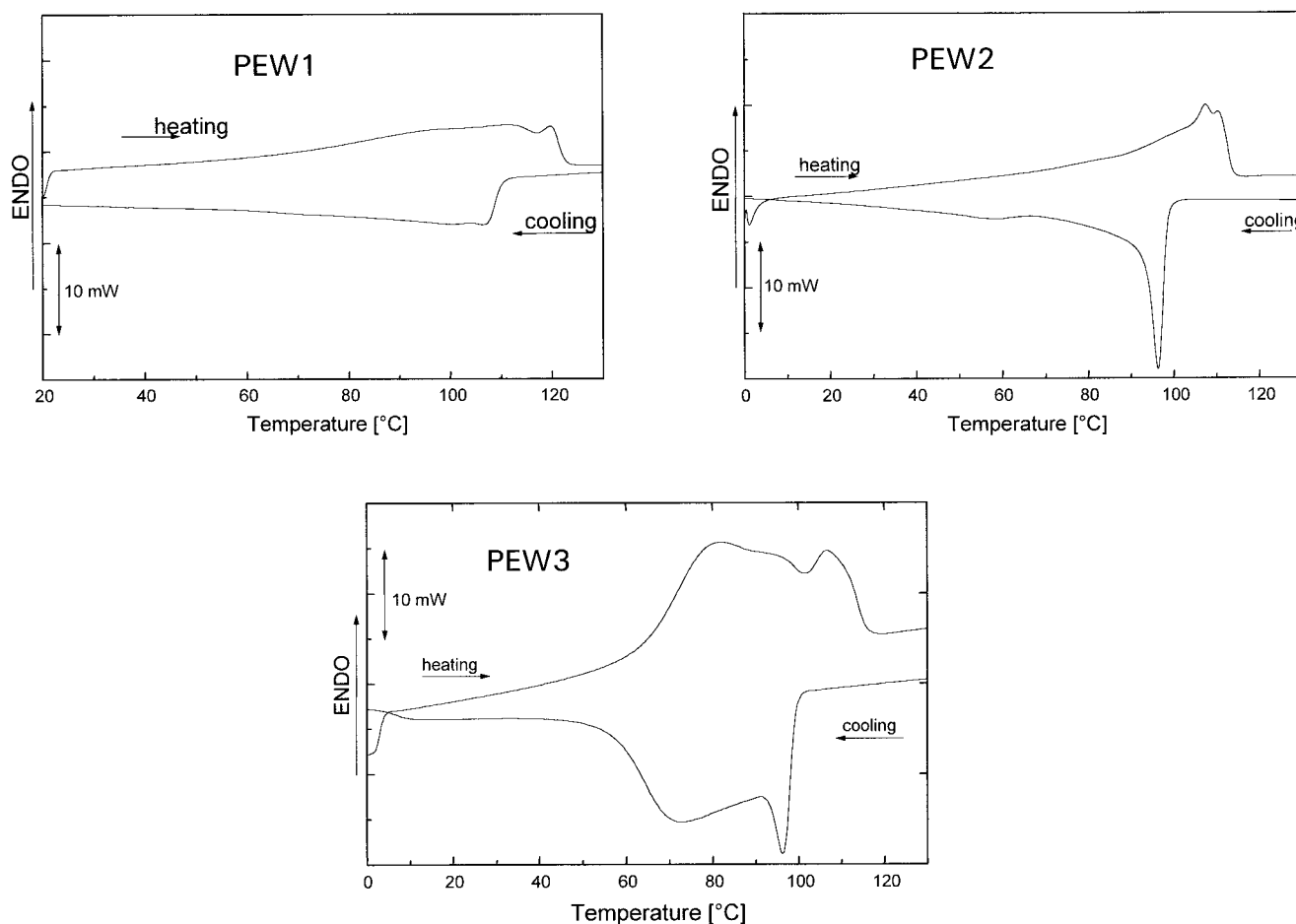
Figure 1 DSC scans recorded during cooling and heating of the different PEW waxes.

temperature (T_c) was taken as the temperature at the onset of the crystallization exotherm. Melting and crystallization extend over a broad temperature range and the melting signals are polymodal. Such a rather complex melting behavior has to be related to the molar mass distribution and to the intermolecular structure distribution.[13] A typical example is the melting of PEW1. This wax has the broadest molar mass distribution and the highest degree of branching. This is reflected in a very broad melting and crystallization

TABLE II
Crystallization and Melting Temperatures and Crystallinity of the Different PEW

| Characteristics	PEW1	PEW2	PEW3
T_m (°C) (DSC, scanning rate: 5°C/min)	125.0	115.5	119.0
T_m (°C) (dilatometry)	120	112	115
T_c (°C) (DSC, scanning rate: 5°C/min)	111.3	101.0	102.2
T_c (°C) (dilatometry)	117.5	105.0	103.5
X_c (DSC)	0.43	0.39	0.76

range. However, this wax has also the highest final melting point, attributed to the presence of a small fraction of more regular chains. (This problem of the relation between molecular structure and molar mass will not be investigated in more detail in this article.) The main interest lies in the characterization of the state in which the PEW is under certain conditions of temperature and concentration. Melting and crystallization that extend over such a broad temperature domain will obviously lead to a strongly temperature dependent crystallinity. The overall crystallinity is obtained from the integration of the melting peaks, using the melting enthalpy of polyethylene. The resulting values are reported in Table II.

"Equilibrium" observations

Crystallization and melting data, as recorded by DSC, depend on the scanning rate. To obtain a correct picture of the transitions that occur under isothermal conditions during polymerization, this effect has to be eliminated: "equilibrium values" at zero scanning rate are needed. They may be obtained in a very accurate
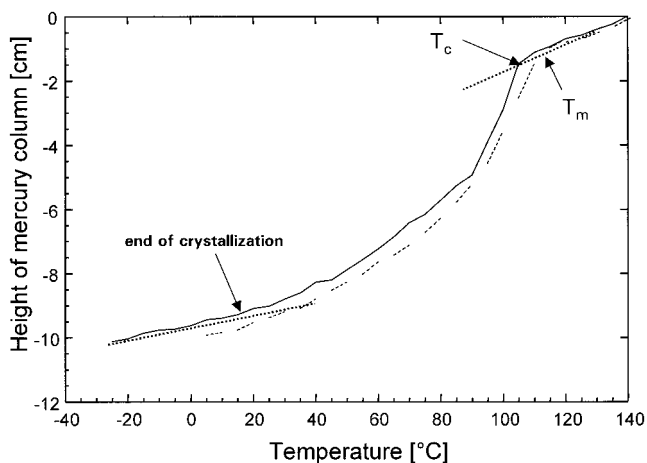
Figure 2 Dilatometric observation of the crystallization and melting of PEW2. — melting; — crystallization.

Figure 3 DSC scans recorded during the cooling and heating of a solution of PEW2 in ST (w_{PEW2} = 0.006).

way by dilatometry. By this technique crystallization and melting are studied by following the volume change as a function of time and temperature. Equilibrium volume data can be obtained at each temperature by isothermal annealing until no change in volume with time is observed any longer. This also allows one to obtain a qualitative indication of the temperature dependency of the degree of crystallinity. (In this investigation, however, no further attempt was made to transform this qualitative information in quantitative data on crystallinity.)
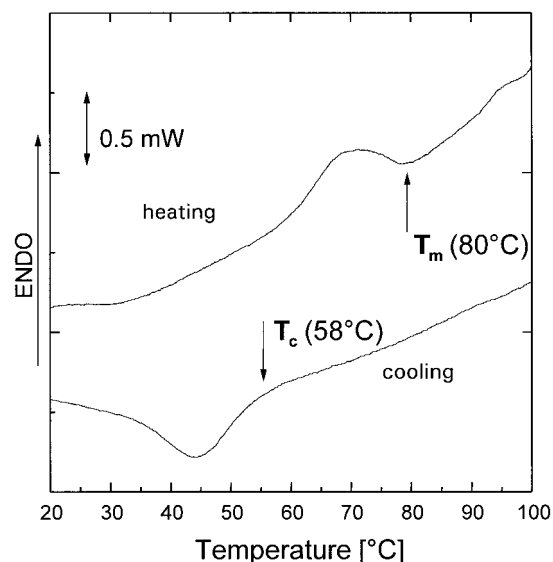
A typical example of the temperature dependency of the volume of PEW2 as obtained by dilatometry is reported in Figure 2. A heating and cooling experiment was performed. The first type of experiment allows one to obtain information on the melting process. The melting point (T_m) corresponds to the temperature at which the very important volume change, which occurs during melting, changes into the linear expansion of the melt. An arrow indicates this temperature. The crystallization temperature is taken as the temperature at which the opposite phenomenon is observed to occur on cooling. An arrow also indicates this temperature. The data are reported in Table II.

Solution behavior of the PEW/ST system

Methodology

To determine the type of phase separation (L-L or L-S phase separation) that is occurring, two techniques were combined: calorimetry and cloud point measurements.

The appearance of an exothermic signal on cooling can be attributed either to crystallization or to L-L phase separation [upper critical solution temperature (UCST)]. Two experimental facts allow distinguishing between crystallization and L-L demixing:

1. The heat of transition involved in crystallization is orders of magnitude larger than the heat involved in L-L demixing.
2. The concentration dependency of the L-L phase separation temperature goes through a maximum at relatively low overall polymer concentration. On the contrary, the onset of crystallization in most situations decreases continuously with decreasing polymer concentration.

Calorimetric investigation of the PEW/ST system

Illustration of the method: PS–PEW2. The calorimetric experiments were performed over the whole PEW2/ST concentration range. On cooling the samples, an exothermic peak was observed and on heating an endothermic peak was recorded. The heat of transition obtained from the integration of the surface of these signals is rather high and is of the order of magnitude of the melting enthalpy of PE. Consequently, the transition is ascribed to the crystallization of PEW2. The temperature at the onset of the exothermic peak is taken as the crystallization temperature T_c, whereas the temperature at the end of the endotherm represents the melting point T_m. A typical example of such a recording is represented in Figure 3.

These temperatures are plotted in Figure 4 as a function of PEW2 concentration. A continuous decrease with increasing styrene content is observed, characteristic for the eutectic crystallization and melting of the PEW2 in the presence of styrene. The solutions were also subjected to cloud point measurements. The obtained cloud points (T_{cp}) coincide very well with the crystallization temperatures. No indication for the occurrence of L-L phase separation was found.
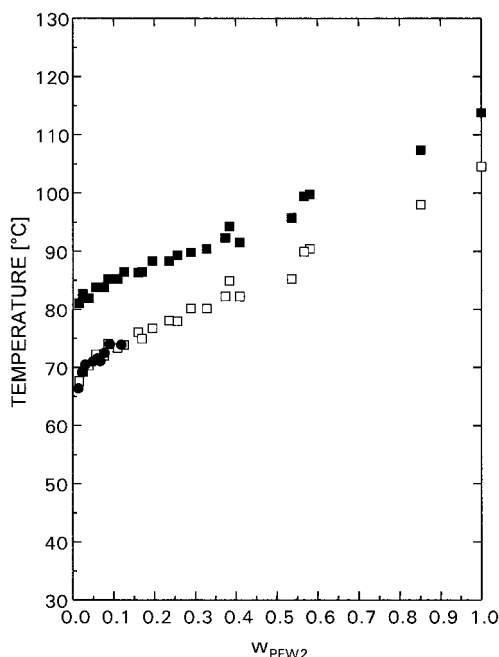
Figure 4 Temperature–concentration diagram for the system ST–PEW. ■ T_m; □ T_c; ● cloud points (CP).

Figure 5 PEW2-concentration dependency of the demixing of PEW2 in the system ST–PS–PEW2 w_{PS} in ST = 0.05. ● T_m; ○ T_c.

One can therefore conclude, because of the absence of L-L demixing, that styrene is a good solvent for PEW2. The system is a homogeneous solution at temperatures above the melting point of PEW2. Cooling results only in crystallization.
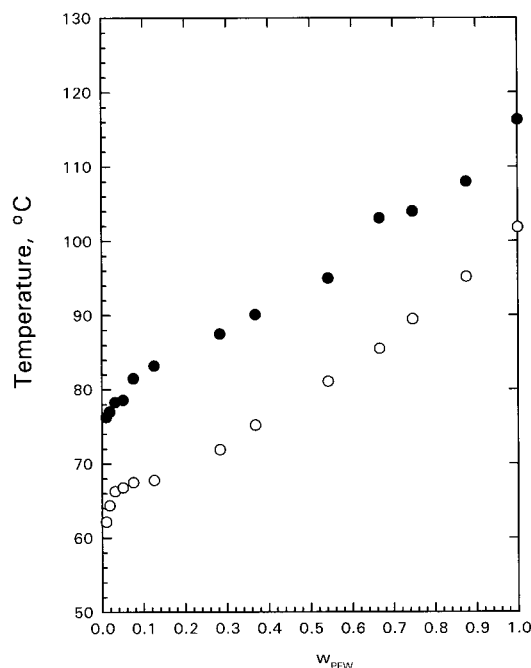
Influence of the type of PEW. The influence of the type of wax was investigated by DSC. The relative positions of T_c and T_m in the temperature–concentration diagram are similar to those observed for the pure waxes. The lower values in the presence of styrene reflect the concentration-induced crystallization and melting point depression.

Solution behavior of the PEW/ST/PST system

The PEW2/ST/PST system

Calorimetric observations. Melting points of PEW2 in a solution of PST in stabilized styrene were measured for different PST contents. Homogeneous solutions could be prepared only at low PEW2 content, although solutions with a higher wax content were nevertheless investigated. The melting point shows a monotonous decrease with decreasing PEW2 concentration. A typical example is represented in Figure 5 for solutions prepared by dissolving PEW2 in styrene with a weight fraction of PST in ST of 0.05. This concentration of ST in PST will be indicated in the text by $w_{PST/ST}$.

Combination of CP measurements and calorimetric observations. Homogeneous solutions of these three-component systems were also investigated by turbidime-

try. The cloud point as a function of PEW2 concentration for different $w_{PST/ST}$ is reported in Figure 6(a)–(d). For each set of experiments $w_{PST/ST}$ was kept constant. These figures also contain the crystallization temperatures derived from the calorimetric observations. No attempt was made to use "equilibrium" values, given that the primary interest lies in the difference between the values of the different transition temperatures and their difference in composition dependency.

The following conclusions may be drawn from these diagrams:

- The phase separation that occurs on cooling the solution in the low PEW2 concentration range corresponds to crystallization: T_c and CP coincide.
- At higher PEW2 content, L-L phase separation precedes crystallization on cooling: the CP values are established at much higher temperature.
- An increase of the PST concentration has only a limited influence on the crystallization temperature.
- The L-L phase separation on the other hand is strongly shifted to lower PEW2 content with increasing $w_{PST/ST}$.

Influence of the type of PEW

The type of wax will influence the demixing processes in two ways. The molar mass will mainly influence the L-L phase separation, whereas the molecular structure
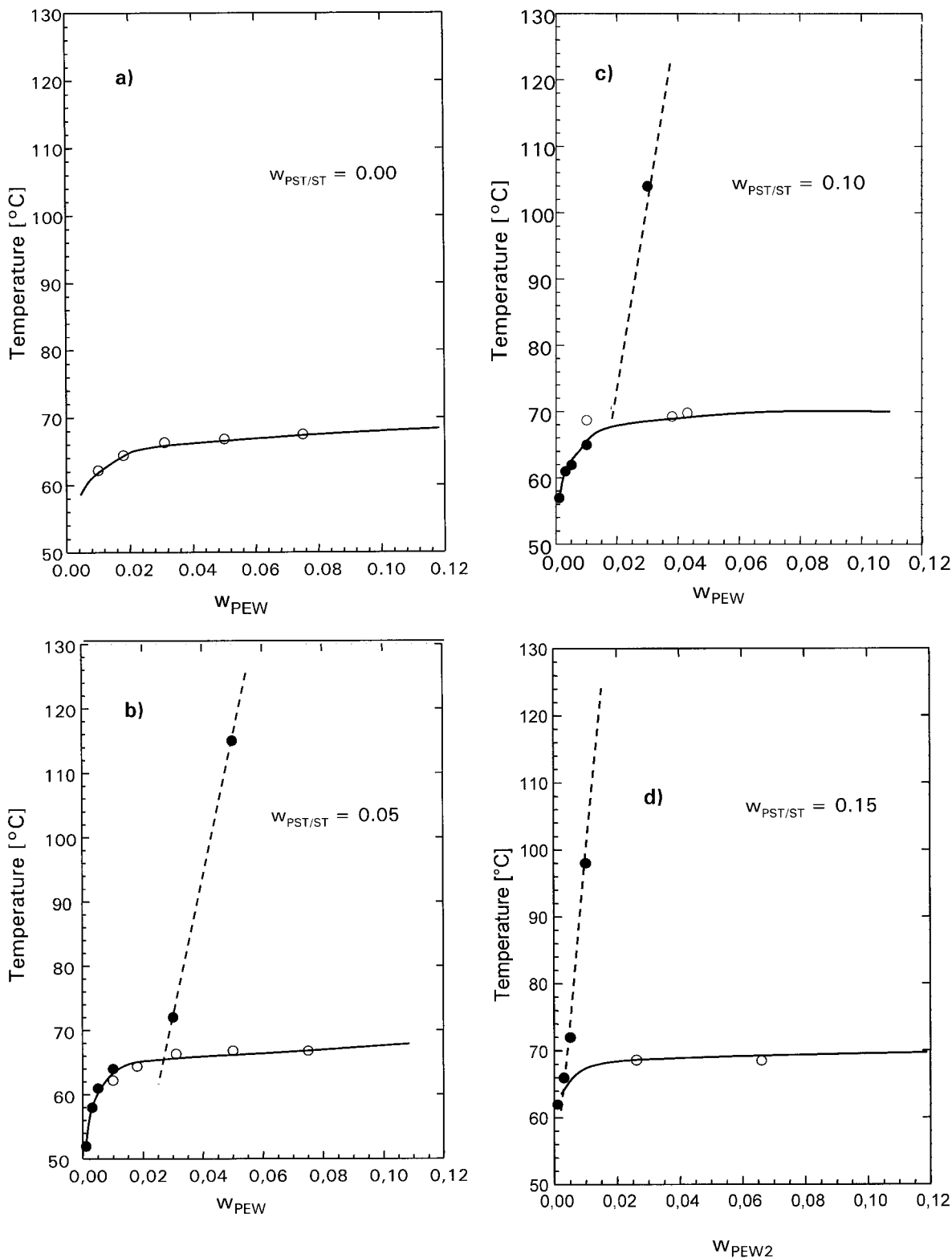
Figure 6 Comparison of crystallization temperatures and L-L phase-separation temperature at different concentrations of ST in PST: (a) $w_{PST/ST} = 0.00$; (b) $w_{PST/ST} = 0.05$; (c) $w_{PST/ST} = 0.10$; (d) $w_{PST/ST} = 0.15$. ○ DSC; ● cloud points.

will mostly affect the L-S transition. These effects are illustrated in Figure 7 for solutions with $w_{PST} = 0.05$. The data can be summarized as follows:

• PEW1 and PEW2 have a rather high molar mass so that L-L phase separation will occur at low PEW concentrations. The main difference be-
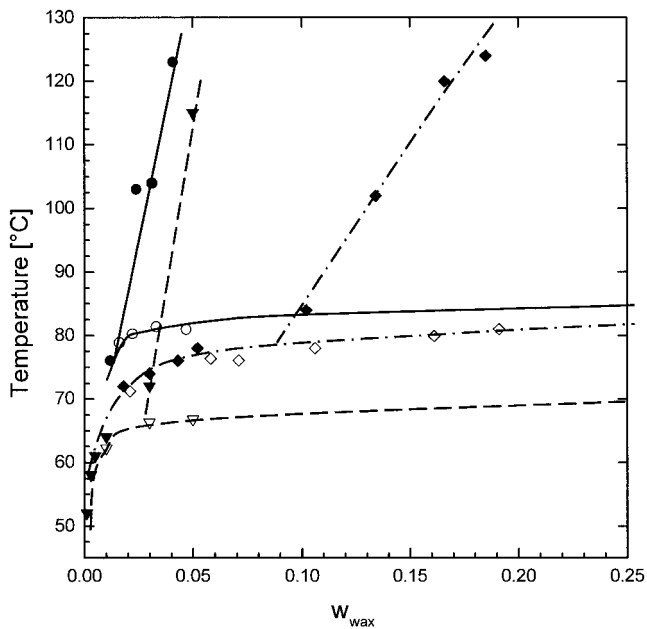
Figure 7 Influence of the type of PEW on the crystallization and L-L phase separation. Closed symbols: CP; open symbols: T_c (DSC). ●, ○: PEW1; ▼, ▽: PEW2; ◆, ◇: PEW3.

Figure 8 Ternary representation at 60°C of the phase-separation behavior of the system ST–PS–PEW. ●: T_c.

tween these two situations is that crystallization of PEW1 sets in at higher temperature than crystallization of PEW2.
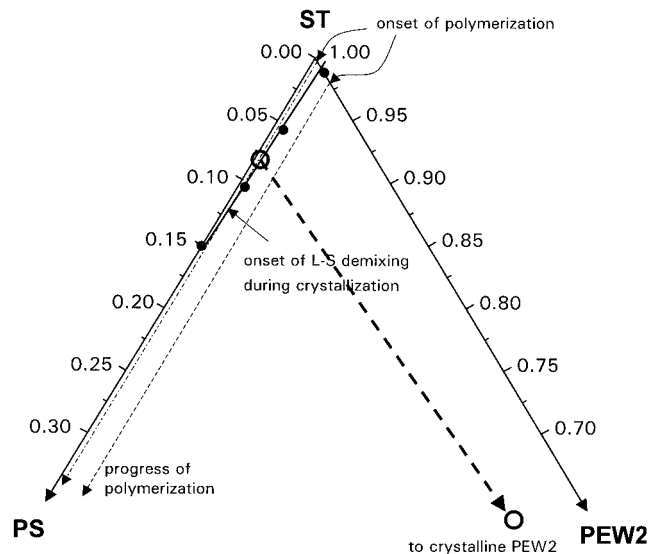
- PEW3 has a much lower average molar mass and therefore L-L phase separation sets in at much higher PEW concentrations.

Ternary representation of the experimental data

General considerations

The quasi-binary data presented in previous sections allow the construction of ternary phase triangles at different temperatures. Two representative temperatures were chosen, 60 and 70°C, for the ST/PST/PEW2 system. The resulting diagrams are represented in Figures 8 and 9.

In these diagrams crystallization temperatures are used. This is strictly speaking not correct because one should conduct the discussion on the basis of equilibrium melting points. Crystallization temperatures, as obtained from the DSC experiments, will nevertheless be used together with the cloud point temperatures. It is indeed well known that crystallization and melting points vary with concentration in almost exactly the same way. Therefore T_c and CP were used because one is interested in what is happening during a polymerization process. These transition temperatures are measured at a certain scanning rate, although isothermal polymerization should correspond to zero scanning rate. Previous experiments, however, have shown that the difference is only a few degrees so that

these dynamic results can be used in a first approximation to illustrate the influence of the experimental parameters on the process.

This discussion is based only on the qualitative representation of the evolution of the demixing domains with temperature in this ternary situation and the interference of these processes, based on the work of Schreinemakers,[14] which have been discussed recently by Koningsveld et al.[15] The purpose of this approach is not to arrive at a quantitative theoretical reproduction of the experimental data.
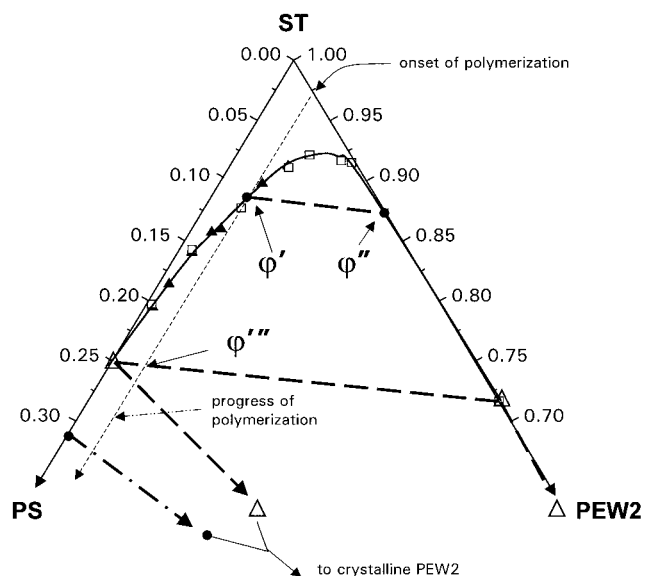
Figure 9 Ternary representation at 70°C of the phase separation behavior of the system ST–PS–PEW. ●— — —●: two-phase equilibrium; △---△---△: three-phase equilibrium.

It is clear from Figure 5 that polymerization without any crystallization can be realized only at a temperature higher than 100°C.

Ternary behavior at 60°C (Fig. 8)

At this temperature homogeneous solutions can be made at only low PEW content. The melting point shifts to lower PEW content with increasing PST content. A two-phase equilibrium (○- - -▶○) will be established between a three-component solution and crystalline PEW2. At $w_{PEW2} = 0.15$, crystallization will interfere with L-L demixing and this will lead to a three-phase equilibrium.

Two different polymerization conditions are simulated and are performed at constant PEW2 content. This means that during the transformation of ST in PST the change in composition of the solution follows a line parallel to the ST–PST axis, starting at the initial concentration of PEW2 in ST (Fig. 8, onset of polymerization).

$w_{PEW2} = 0.004$ (Fig. 8, – - –▶). When the weight fraction of PST formed is $w_{PST/ST} = 0.12$, crystallization will set in and PEW2 is separated as crystalline domains. This point is indicated in Figure 8 by "onset of L-S phase separation." From $w_{PST/ST} = 0.15$, crystallization of PEW should be almost completed and a solution of ST in PST should be in equilibrium with crystalline PEW. However, this will not be the case because at 60°C only part of the PEW will have crystallized. The dilatometric and DSC data reported earlier clearly indicate that such complete crystallization can be realized only by cooling to low temperature. This will result in a much more complex phase relation with the possibility of establishing a three-phase equilibrium as a consequence of the interference of L-L phase separation with crystallization.

$w_{PEW2} = 0.004$ (Fig. 8, - - ▶). The polymerization sets in from a heterogeneous system in which PEW2 is partially crystallized. Because of this limited extent of crystallization at this temperature, interference with L-L phase separation is also expected to proceed at a certain degree of conversion.

Ternary behavior at 70°C

The situation is different because now L-L demixing predominates at any PEW2 content. L-S phase separation can be observed as the first transition only at the ST–PEW2 axis ($w_{PEW2} \approx 0.20$).

When polymerization is carried out with $w_{PEW2} = 0.04$ (- - -▶), L-L demixing occurs when about 10% of styrene (at φ') has been transformed in polystyrene. This phase separation will lead to the coexistence of a solution containing almost only PEW2 and styrene (φ'') and one that contains mainly styrene, polystyrene, and a very small fraction of PEW2 **(φ')**. Strictly speak-

ing, this representation of the situation is correct only when the polymer is monodisperse. However, this approach can nevertheless be used in a first qualitative approximation. The tie line is only schematic, given that no information is available on the composition of the coexisting phase φ''.

During the continuation of the polymerization, the PST content will increase so that at a certain point L-L phase separation will interfere with crystallization of PEW2. Such interference will establish a three-phase equilibrium. This can occur when, for example, the situation φ''' will be reached. Here also the tie line is drawn schematically and is not based on the experimental determination of the coexisting concentrations. At this point a three-phase equilibrium (Fig. 9, △) between two solutions with different compositions and crystalline PEW2 will be established. One of them will contain almost only PEW2 and ST, whereas the other one is mainly composed of ST and PST. Once φ''' has crossed the three-phase triangle, a two-phase equilibrium will persist between a solution of ST/PST and crystalline PEW2 (Fig. 9, ● – – – ●). This type of equilibria has been discussed in the literature.[14,15] Here also only a fraction of PEW will have crystallized at this temperature.

Demixing processes during polymerization: PIPS

The data reported in the previous sections allow us to draw conclusions concerning the different thermal transitions that occur during the polymerization of styrene in the presence of PEW. Factors that have to be taken into account are the PEW concentration, the type of PEW, and the temperature of polymerization. Observations made during the polymerization of ST in the presence of PEW should lead to the same conclusions. To verify this agreement, demixing will be followed during the polymerization of ST in the presence of PEW (TIPS). The problem will be illustrated for the PEW2/ST/PST system.

At a certain degree of conversion at a well-defined temperature, the ratio of ST/PS will be such that L-L phase separation will set in. This transition point has to correspond to the one obtained by cooling of a solution containing the same components at the same concentration. A very convenient method to investigate such a combination of phenomena is dilatometry. This technique allows, in one experiment, the determination of the kinetics of the polymerization, the degree of conversion, and the onset of L-L demixing during this polymerization.
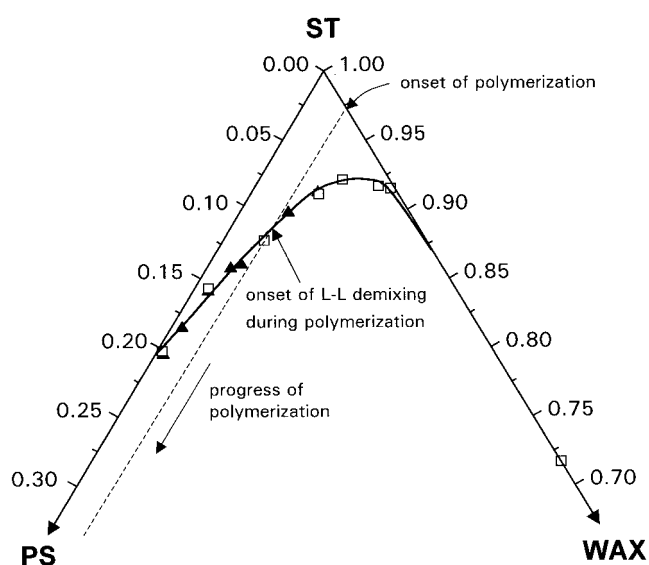
A typical example of this kinetics is given in Figure 10 for a polymerization carried out at 90°C for different PEW2 contents. At this temperature and in the range of polymerization considered, only L-L phase separation occurs. The progress of the degree of conversion is linear as a function of time and the PEW2
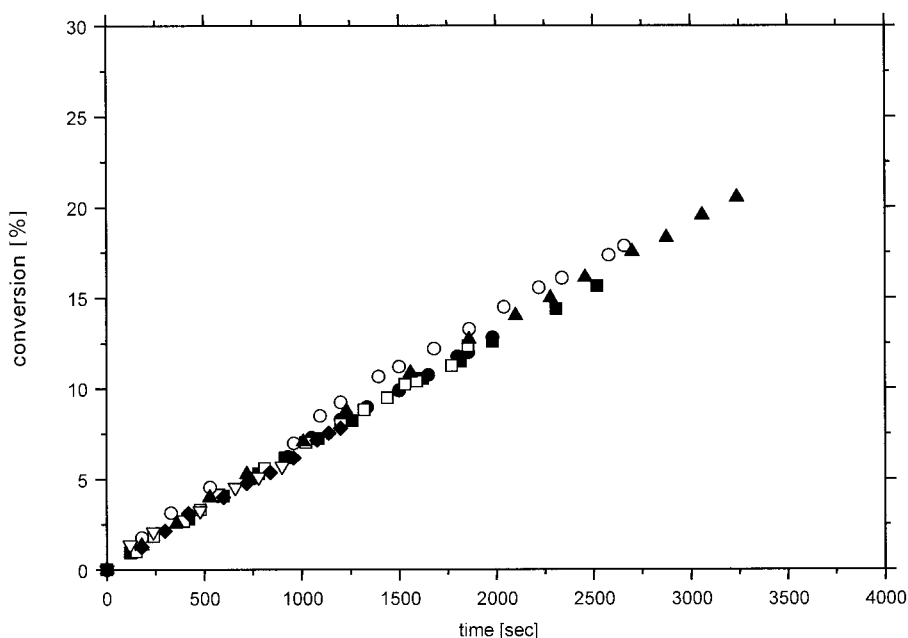
Figure 10 Kinetics of polymerization of styrene in the presence of different amounts of PEW. w_{PEW}: ▲ 0.0053; □ 0.010; ○ 0.02; ▼: 0.040.

content has no influence. This PEW2 content also does not influence the degree of polymerization. Typical values of number- and mass-average molar mass are 3.8×10^4 and 6.7×10^4, respectively. The combination of these data with the time needed to reach the onset of L-L demixing allows the construction of a ternary phase diagram like the one represented in Figure 11. The data obtained by TIPS were derived from the quasi-binary representations reported earlier. The agreement between the two approaches is very good.

L-L demixing at w_{PEW} = 0.025, for example, will set in when the dotted line intersects with the cloud point line (solid line in Fig. 11). An arrow indicates this point.

CONCLUSIONS

The objective of this investigation was the study of the demixing processes that occur during the polymerization of styrene in the presence of a polyethylene wax. It has been shown that this problem can be approached in two ways.

- TIPS allows for the construction of a ternary phase diagram clearly delimiting the L-L and the L-S phase-separation domains. At low temperature, most of the ternary triangle is occupied by the L-S phase separation. L-L demixing, on the contrary, dominates at higher temperature.
- A similar diagram can be constructed by PIPS. The simultaneous observation of the progress of polymerization and L-L demixing also leads to the same ternary diagram.
- This approach allows a decision on which type of demixing occurs under certain polymerization conditions like temperature, type of PEW, and PEW content. During polymerization at constant temperature L-L phase separation can eventually occur in combination with crystallization. Because of the broad crystallization temperature range, PEW will be crystallized only partially. Complete

Figure 11 Ternary behavior of the polymerizing system SP–PS–PEW at 90°C. □ TIPS; ▲ PIPS.

crystallization can occur only on cooling to low enough temperature.

- The combination of these different phase transitions will result in a specific morphology of size and distribution of the PEW domains in the polymerized matrix.

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