Spinodal decomposition induced by copolymerization in the mixture of methyl methacrylate/vinyl acetate/poly[ethylene-co-(vinyl acetate)]

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SUMMARY: Phase separation during copolymerization of a mixture of methyl methacrylate/vinyl acetate/poly[ethylene-co-(vinyl acetate)] (MMA/VAc/EVA) is investigated by time-resolved light scattering (TRLS) and scanning electron microscopy (SEM). TRLS investigation shows that a phase separation takes place via spinodal decomposition (SD) when polymerization in a mixture of MMA/VAc/EVA as well as of MMA/EVA proceeds. Scattering profiles with double-peak feature develop in the case of SD induced by copolymerization in MMA/VAc/EVA mixtures, whereas only a single peak occurs in the MMA/EVA copolymerization. Moreover, it is shown that the process of SD during polymerization is different from that in ordinary thermally-induced SD, i.e. \( q_m \), the wavenumber \( q \) at the peak position of the scattering profile, remains virtually invariant with time. SEM observation show that the unique morphologies are obtained ultimately during SD induced by polymerization in MMA/EVA and MMA/VAc/EVA mixtures. For the polymerized MMA/EVA mixture, PMMA-rich particles with a uniform size and distribution are dispersed in the matrix of an EVA-rich phase, whereas for polymerized MMA/VAc/EVA mixtures, MMA-V Ac copolymer rich particles are finely dispersed in an EVA-rich phase as matrix with bimodal distribution of sizes, i.e. uniform small domains and larger domains are obtained simultaneously, which is consistent with the results of the double peak observed in light scattering profiles.

Introduction

Due to the importance not only in a purely scientific viewpoint but also in the design and control of structure and properties of multicomponent polymer systems, spinodal decomposition (SD) induced by a temperature jump from the one- into the two-phase region has been extensively investigated by experiments, theory, and computer simulations\(^1,2\). SD is an unstable and spontaneous process that occurs due to the instability at an infinitesimal composition fluctuation. As a result of SD, a highly interconnected two-phase morphology with a unique periodicity or domain structures with relatively narrow size distributions are obtained\(^3\). A control of the morphology becomes feasible, since the characteristic morphology can be fixed or frozen by quenching the demixed system below the glass transition temperature (\( T_g \)) after an appropriate period of phase separation.

However, for materials design under practical aspects, SD induced by chemical reaction may be more interesting. This is typically illustrated by the polymerization of monomer A in the presence of polymer B. For example, polybutadiene (PB) is soluble in monomeric styrene and the PB/styrene mixture is initially a single-phase system at the polymerization temperature (100°C). The system will be thrust into the two-phase regime as the polymerization proceeds to form polystyrene, and this elevates the upper critical solution temperature (UCST). Hence, an SD is expected to take place. High impact polystyrene (HIPS) and acrylonitrile/butadiene/styrene (ABS) resin are the most commercially significant examples produced in this way\(^4\). However, agitation is usually applied during the polymerization, so that it is very hard to analyze the SD process under a complicated shear field.

Meanwhile, polymerization-induced SD is also frequently employed to prepare polymer dispersed liquid crystals (PDLCs) films, which are composed of microdroplets of liquid crystals finely dispersed in a polymer matrix\(^5\). Such films can be electrically switched between a strongly scattering “off” state and a highly transparent “on” state. Therefore, they are of potential use in electro-optical devices, such as shutters, switches and displays. A preferred method to prepare these films is to polymerize an initially homogeneous mixture of monomers or prepolymers and the liquid crystals (LC). As the polymerization proceeds, the solubility of the LC in the mixture decreases, leading a to phase separation which can occur via SD. By polymerization-induced SD, PDLCs materials with a morphology of nearly uniform dispersed of liquid droplets can usually be obtained. Furthermore, it allows a better control of the morphology, which is considered to be a key parameter for the electro-optical behavior of...
PDLCs, by choosing the temperature and the rate of polymerization.

Therefore, understanding the dynamics of SD induced by polymerization may have significant industrial importance in controlling the morphology of phase-separating materials. In a previous publication\(^5\), the phase separation during the static polymerization in an 80/20 (w/w) methyl methacrylate/poly[ethylene-co-(vinyl acetate)] (MMA/EVA) mixture was studied and the nature of the SD was identified. Moreover, it was shown that the characteristics of the dynamics of SD induced by polymerization in this system are different from those in familiar thermally induced SD during isothermal annealing after a temperature jump, i.e. the wavenumber \(q_u\) of maximum intensity in light-scattering profiles remains constant with time for a quite long period even in the intermediate or late stages of SD. The materials produced in this way have the unique two-phase structure in which PMMA particles with a uniform size are regularly dispersed in an EVA matrix, even when EVA is the minor component (e.g. 20 wt.-%). Moreover, these materials exhibit excellent mechanical properties, such as high impact-strength, high Young’s modulus and a high heat-resistance close to that of PMMA\(^7\). In the previous paper\(^6\), the effect of poly(methyl methacrylate)/poly(vinyl acetate) (PMMA/PVAc) graft copolymers on the dynamics of SD induced by polymerization in this system was also investigated. PMMA/PVAc graft copolymers were obtained during the polymerization by adding a poly(vinyl acetate) (PVAc) macromonomer with a methacrylate end-group. It was shown that the existence of a small amount of the copolymer suppresses the demixing at the early stages of SD and delays the structure coarsening. Thereby, phase separation can be manipulated by a graft copolymer incorporation.

In this paper, we report on experimental results of studies on the SD induced by polymerization in the system methyl methacrylate/vinyl acetate/poly[ethylene-co-(vinyl acetate)] (MMA/VAc/EVA). Practically, copolymerization is frequently employed to control the properties of materials produced by phase separation induced by polymerization\(^4\). For example, ABS resins are produced by the copolymerization of styrene with acrylonitrile in the presence of PB; modified ABS (so-called high heat-resistance ABS) is obtained by the copolymerization of either \(\alpha\)-methylstyrene, methacrylonitrile, or \(N\)-phenylmaleimide with styrene and acrylonitrile in the presence of PB; methyl methacrylate/butadiene/styrene (MBS) resins, which exhibit high transparency and high impact strength, are produced by the copolymerization of styrene with methyl methacrylate in the presence of PB, etc. However, the dynamics of an SD induced by copolymerization have not been fully investigated yet. Therefore, the understanding of SD induced by copolymerization is of great interest in both industrial application and academic research. The main aim of this study is to get insight into the characteristics of SD induced by copolymerization, the effects of copolymerization on the dynamics of SD and the process of structure development. We believe that this approach will lead to a more thorough view of SD induced by polymerization.

**Experimental part**

Poly[ethylene-co-(vinyl acetate)] (EVA), produced by Bayer Co., contains 40 wt.% vinyl acetate and has a number-average molecular weight \(M_n\) of \(1.4 \times 10^5\) and a molecular weight dispersity \(M_w/M_n\) of 1.95. The commercial monomers methyl methacrylate (MMA) and vinyl acetate (VAc) were purified by distillation under reduced pressure after the inhibitor was removed by a conventional method. The initiator \(2,2'-\text{azoisobutyronitrile (AIBN)}\) was used after purification by recrystallization from absolute ethanol.

Four mixtures MMA/VAc/EVA with weight compositions of 90/0/10, 80/10/10, 70/20/10 and 60/30/10 were studied. EVA and AIBN (0.6 wt.-%) were dissolved in MMA and VAc monomers at ambient temperature and the polymerization was performed at 60 °C.

The specimens for light-scattering measurements were prepared as follows: the mixtures were sealed in a cell comprising two cover glasses and an aluminium spacer of thickness 0.05 mm with the aid of an epoxy adhesive (details have already been described in the previous paper\(^6\)).

Light-scattering measurements during polymerization were conducted on our homemade time-resolved light scattering (TRLS) apparatus. The principle of the apparatus was described in some earlier papers\(^6\), here we only mention the parts relevant to the present study. Fig. 1 shows the setup of our TRLS apparatus. The light source is a 15 mW plane-polarized He-Ne laser with a wavelength of 632.8 nm. The sample sandwiched between two cover glasses was inserted into a heating chamber kept at a constant temperature with an accuracy of ±0.1 °C. The chamber was set horizontally on the light-scattering stage as shown in Fig. 1. Radiation from

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**Fig. 1.** Experimental setup of the time-resolved light scattering apparatus
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the He-Ne gas laser was applied vertically to the specimen. The light scattering profile \( I(q) \) (relative scattered intensity \( I \) versus scattering vector \( q \)) under a Vv (parallel polarized) optical alignment was determined using a two-dimensional CCD-camera detector with \( 512 \times 512 \) pixels and intensity resolution of 256 levels. The magnitude \( q \) of the scattering vector \( q \), corresponding to the wavenumber of concentration fluctuation, is defined by

\[
q = \frac{4\pi}{\lambda} \sin(\theta/2)
\]

where \( \theta \) is the scattering angle and \( \lambda \) the wavelength of the laser in the sample. The changes of the light scattering profile were recorded at appropriate time intervals during isothermal annealing (polymerization).

The degree of conversion was estimated by differential scanning calorimetry (DSC) (Shimadzu7A-50I) according to the area of the exothermic peak evolving from the polymerization during isothermal runs at 60°C.

The two-phase morphology of the polymerized specimens was observed by scanning electron microscopy (SEM) (Hitachi HU-11B). The specimens were fractured in liquid N\(_2\) and etched in a mixture solvent of 3/1 (v/v) cyclohexane/toluene to remove the EVA-rich phase. Then the etched surface was investigated by SEM.

Results and discussion

Phase separation by TRLS

Using an optical microscope, the mixture of MMA/VAc/EVA initially appears homogeneous. After a certain time lag, a two-phase structure with low contrast appears and the contrast becomes higher with increasing polymerization time.

Fig. 2–5 show the time-resolved light scattering profiles during polymerization at 60°C for four mixtures of MMA/VAc/EVA with weight compositions of 90/0/10, 80/10/10, 70/20/10 and 60/30/10, respectively.

For the mixture of 90/0/10 MMA/VAc/EVA (Fig. 2), no appreciable light scattering was detected from the mixture in the early stages of polymerization. A peak in the light scattering profile appears after about 15 min, indicating the occurrence of SD and the development of a regularly phase-separated structure with the dominant wavelength \( \Lambda_\text{m} = 2\pi/q_\text{m} \), where \( q_\text{m} \) is the peak scattering vector. From Fig. 2, one can immediately notice that the peak scattering vector \( q_\text{m} \) shifts very slightly toward smaller angles only in the early stages, and then remains constant with time. In the meantime, the peak intensity \( I_\text{m} \) increases continuously with time and eventually becomes invariant after about 50 min.

The time-evolution of the profiles in this case is obviously distinguished from that of an isothermal SD in the absence of polymerization. The isothermal SD in a binary mixture of polymer A and polymer B is often divided into three stages\(^9\). In the early stage, periodic concentration fluctuations with dominant wavelength \( \Lambda_\text{m} = 2\pi/q_\text{m} \) are developed and \( q_\text{m} \) remains virtually invariant. The growth of the scattering intensity can be described with an exponential function of time as predicted by the linearized theory of Cahn-Hilliard\(^9\), when the nonlinear term in the diffusion equation describing the time dependence of the amplitude of concentration fluctuation may be neglected. In this stage, \( q_\text{m} \) values are determined by the thermodynamic driving force for phase separation characterized by the quench depth \( |\chi - \chi_s| \), i.e.

\[
q_\text{m} \propto |\chi - \chi_s|^{1/2}
\]

where \( \chi \) and \( \chi_s \) are the Flory-Huggins segmental interaction parameters of polymer A and polymer B at the phase separation state and the spinodal point, respectively\(^9\). In the intermediate stages, both \( q_\text{m} \) and \( I_\text{m} \) grow with time, i.e. \( q_\text{m} \) decreases and \( I_\text{m} \) increases; in the later stages, the compositions of the two phases reach equilibrium and both \( \Lambda_\text{m} \) and the size of the demixed structure grow with time, which is due to a coarsening of the phase-separated structures to minimize their free energy by minimizing the interfacial areas. However, this conventional picture has been already altered by the presence of a polymerization, i.e. \( q_\text{m} \) is almost constant with time for the case of 90/10 MMA/EVA as shown in Fig. 2.

It should be noted that such behavior, i.e. a time independence of \( q_\text{m} \), has also been observed for an SD induced by curing reaction in an epoxy/ATBN/Versamid mixture\(^10\) and for a polymerization-induced SD in an 80/20 (w/w) MMA/EVA mixture\(^6\). A plausible interpretation for this time variation of \( q_\text{m} \) in the present system may be described qualitatively as follows\(^11\): From the linearized theory in the early stages, \( q_\text{m} \) is given by Eq. (2). Because the present system can be considered as a ternary polymer solution consisting of PMMA, EVA and a solvent (MMA monomer), when MMA is polymerized to yield PMMA, Eq. (2) can be rewritten as:
where $\phi_p$ and $\phi_s$ are the total volume fraction of the polymer at phase separation and the spinodal volume fraction of the entire polymer, respectively. $\phi_p$ is fixed for a given system while $\phi_s$ increases with polymerization, leading to a continuous increase of the quench depth with polymerization of MMA, i.e., the larger the quench depth, the larger $q_m$. Therefore, the polymerization should cause a shift to larger $q_m$. On the contrary, the phase-separated structure should be coarsened due to the interfacial instability leading to smaller $q_m$. The time independence of $q_m$ in the present system may be due to a balance of both thermodynamic driving forces, namely the growth of the unstable concentration fluctuations with long wavelength is suppressed by an increase in the quench depth. It should be noted that a linearized theory is expected to be applicable only in the very early stages of SD. However, the effect of an increase in the quench depth on the phase-separation behavior may be qualitatively described according to Eq. (2) or (3), because the linear term in the diffusion equation in this case may still be dominant.

For the mixture of 80/10/10 MMA/VAc/EVA (Fig. 3), qualitatively the same behavior occurs. The scattering peak starts to develop at about 16 min, the peak also shifts very slightly toward smaller angles only in the early stages and then remains constant with time. In the meantime, the intensity of the peak increases continuously with time and eventually becomes invariant after about 30 min. However, one can notice that the intensity around larger $q$ ($\approx 3.5 \mu$m$^{-1}$) grows further even after the peak intensity becomes invariant. This is obviously different from that for 90/0/10 MMA/VAc/EVA mixture as seen from Fig. 2, in which the increase of intensity over the whole $q$ range stops simultaneously. It seems that a secondary peak (despite of only a weak shoulder here) is developed at larger $q$ with increasing copolymerization. This may imply that domains with shorter wavelengths are developed as well as the dominant domains with larger wavelengths.

For the mixture of 70/20/10 MMA/VAc/EVA (Fig. 4), pronounced double peaks in the scattering profiles are developed. A dominant peak at smaller $q$ is developed at about 18 min and a secondary peak at a larger $q$ can be observed clearly after about 50 min of polymerization. The peak intensity at smaller $q$ grows continuously until 80 min and then becomes invariant, while the intensity of the peak at larger $q$ grows further until 150 min. Eventually, the scattering profile becomes invariant after 150 min over the whole range of $q$.

For the 60/30/10 MMA/VAc/EVA mixture (Fig. 5), scattering profiles with the features of strongly pronounced double peaks are observed. The dominant peak at smaller $q$ appears at about 20 min. The peak intensity grows continuously until 80 min and then becomes invariant, while the secondary peak at larger $q$ emerges at
about 60 min and its intensity grows further until 150 min. Eventually, the scattering profiles become fixed at 120 min.

By comparing the time-evolution of the scattering profiles of a 90/10 MMA/EVA mixture with that for the MMA/VAc/EVA mixtures, one can see similarities and differences. As a similarity it is found that SD occurs in all cases, demonstrating that regularly phase-separated structures can be developed by this way. The position of the dominant peak is nearly independent of time in all cases, which is referred to the interplay of phase separation and polymerization. As a difference it is found that the scattering profiles with double peak features are developed in the case of an SD induced by copolymerization in the MMA/VAc/EVA mixtures, whereas only a single peak is observed for the MMA/EVA mixture.

The development of a double peak in the scattering profiles during SD induced by copolymerization may be due to the significant composition drift of the MMA/VAc copolymers during copolymerization. It is noted that the reactivity ratios of the monomers, \( r_1 \) and \( r_2 \), for MMA and VAc, respectively, are of different size, viz. \( r_1 = 24.02 \), \( r_2 = 0.03 \). Hence, the VAc content in the MMA/VAc copolymer will deviate significantly from its feed content. Moreover, such deviations will become more significant with proceeding polymerization especially during later stages.

The secondary peak appears at a fairly late stage, indicating that its corresponding phase separation takes place under an extremely deep quench. According to Eq. (3), a larger quench depth leads to a larger \( q_m \). Hence, the secondary peak appears at a higher \( q \). The scattering profiles with double-peak features during SD induced by copolymerization suggest that multiple distributions of phase-separated structures with different sizes are obtained in these cases.

**Time-evolution of structure during polymerization**

Because the secondary peak at larger \( q \) in the case of SD induced by copolymerization remains only a weak maximum in the light scattering profiles compared to the dominant peak, we focus our attention on the time-changes of the dominant peak scattering vector \( q_m \) and the peak intensity \( I_m \) for the four mixtures.

Fig. 6a and 6b show the time-dependence of the peak scattering vector \( q_m(t) \) and the peak intensity \( I_m(t) \) on a double-logarithmic scale for the four systems. The data of \( I_m(t) \) for the four systems are shifted vertically for viewing clarity. Fig. 6c shows the time dependence of the conversion on a semi-logarithmic scale.

From Fig. 6a, it can be seen that \( q_m(t) \) is nearly independent of time in each case. However, the levels of \( q_m \) in the \( q_m(t) \) vs. \( t \) curves are effectively affected by the ratio of the monomers MMA and VAc in mixtures. When the content of VAc increases, the levels of \( q_m \) in \( q_m(t) \) vs. \( t \) curves shift down. The reason why the level of \( q_m \) becomes smaller when the VAc content increases has not been completely clear. However, one interpretation can be given as follows: The levels of \( q_m \) for each case can be considered to be determined mainly by the \( q_m \) values at the early stages rather than by the time-dependence, because of the time-independence of \( q_m(t) \) in all cases. According to Eq. (3), the \( q_m \) values at early stages are proportional to \( |\phi_p - \phi_v|^{1/2} \). From the results of the time-dependence of the conversion shown in Fig. 6c, it can be seen that phase separation occurs almost in the same range of conversion (about 2%), irrespective of the difference in the composition of MMA/VAc, demonstrating that \( \phi_p \) is almost the same. \( \phi_v \) in Eq. (3) is a spinodal total volume fraction of the polymer below which the mixture is miscible and above which the mixture is immiscible. Obviously, \( \phi_v \) is dependent on \( \chi_{AB}^{1/2} \), i.e. the smaller \( \chi_{AB} \).
the larger $\phi_v$. It is reasonable that the $\chi_{ab}$ between EVA and MMA/VAc copolymers decreases with increasing VAc content in MMA/VAc, because of the common monomer VAc of the EVA and the MMA/VAc copolymers. The decrease of $\chi_{ab}$ results in an increase of $\phi_v$ that leads to the decrease of the levels of $q_m$.

In Fig. 6b, it is shown that $I_m(t)$ in each case increases rapidly with time in the early stages, and slows down significantly in the succeeding time region, until it eventually levels off. This indicates that the rate of phase separation in the early stages is larger and then becomes smaller with increasing polymerization.

Fig. 6c shows that (in all cases with the same content of initiator) the polymerization initially proceeds almost with the same rate irrespective of changes of the monomer ratios in the mixtures, indicating that the reactions are controlled by the rate of initiation. As the conversion increases, the reaction becomes transitional diffusion-controlled and the resulting decrease in the termination rate, which is due to the increasing viscosity of the reaction medium, causes the autoacceleration or gel effect. The more VAc there is in the system, the later the autoacceleration starts, which can be attributed to the lower reactivity of the VAc monomer.

Combining the results of Fig. 6b and 6c, it can be seen that the time-dependence of the phase-separation rate for each case is related to its rate of polymerization. The time range over which the phase separation slows down is consistent with an autoacceleration of the polymerization or a gelation. Hence, the slowing-down of the phase separation with time can be referred mainly to an increase of viscosity in the reaction medium. The larger rate of phase separation in the early stages and the leveling off of the phase separation can be referred mainly to the low viscosity and to the vitrification of the reaction medium, respectively.

Fig. 6b also shows that $I_m(t)$ in the early stages can be expressed approximately by a power relation

$$I_m(t) \propto t^b$$

The values of $b$ were estimated as 6.4, 5.1, 4.4 and 3.2 for different MMA/VAc/EVA mixtures with respective compositions 90/0/10, 80/10/10, 70/20/10 and 60/30/10. Obviously, the $b$ values strongly depend on the feed ratio of MMA/VAc, i.e. $b$ decreases with increasing VAc contents, indicating a decrease of the phase-separation rate. It is known that the phase separation rate depends not only on the mobility of the components but also on the thermodynamic driving force for separation. As has been discussed above, the thermodynamic driving force can be considered to decrease with increasing VAc content in MMA/VAc copolymers, which leads to decreasing $b$ values.

**Fig. 7.** Scanning electron micrographs of the fractured surfaces of samples under spinodal decomposition induced by polymerization at 60°C for MMA/VAc/EVA mixtures with the following weight compositions: (a) 90/0/10, (b) 80/10/10, (c) 70/20/10, (d) 60/30/10

**Morphology by electron microscopy**

Fig. 7a–d show the SEM micrographs of polymerized samples of the four mixtures. As has been mentioned in the Experimental part, the fractured surface was etched with a mixture of 3/1 (v/v) cyclohexane/toluene, which is a good solvent for EVA but not for PMMA and MMA/VAc copolymers. Hence, EVA can be washed out by etching and then the remaining particles mainly consist of PMMA or MMA/VAc copolymers. In Fig. 7a (90/0/10 MMA/VAc/EVA), the morphology clearly shows spherical domains with fairly uniform size around 10 µm dispersed quite regularly in a matrix of EVA.

Fig. 7c–d show a bimodal distribution of particle sizes, which is obviously different from that in the MMA/VAc system. Besides particles with about 10 µm diameter, smaller particles with a size of about 1 µm can be seen as well. The bimodal morphology is obviously in agreement with the result of double peaks emerging in the light scattering profiles. The dominant peak at smaller $q$ can be
assigned to the interdomain spacing between the larger particles, and the secondary peak at larger \( q \) can be assigned to the overall spacing.

These results demonstrate that unique morphologies are ultimately obtained during SD induced by polymerization in MMA/EVA and MMA/VAc/EVA mixtures. For polymerized MMA/EVA mixtures, a morphology of PMMA-rich particles with a uniform size and distribution dispersed in the matrix of an EVA-rich phase is obtained, whereas for polymerized MMA/VAc/EVA mixtures, MMA/VAc copolymer-rich particles are finely dispersed in the matrix of an EVA-rich phase with a bimodal distribution of sizes, i.e. uniform small domains are obtained simultaneously with the uniform large domains.

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