

Fluorescence Method for Studying Latex Film Formation

Önder Pekcan and Şaziye Uğur

Department of Physics, Istanbul Technical University, 34469 Maslak, Istanbul, Turkey

(Received 14 March 2003)

Latex films were prepared separately by annealing pyrene (P_y) labeled poly (methyl methacrylate) (PMMA) particles above the glass transition temperature. The variation in the direct fluorescence emission of excited pyrene from labeled latex films was monitored as a function of annealing temperature. Void closure temperature (T_c) and time (t_c) were determined at the point where the fluorescence emission intensity becomes maximum. Below this point, increase in fluorescence intensity (I_{0P}) against temperature was used to determine the activation energy for viscous flow ($\Delta H \cong 47$ kcal/mol). Decrease in I_{0P} above the void closure temperature was used to produce the backbone activation energy ($\Delta E \cong 44$ kcal/mol) for the interdiffusing chains.

Keywords: Fluorescence, interdiffusion, void closure, latex.

1. Introduction

The term “latex film” normally refers to a film formed from soft latex particles (T_g below room temperature) where the forces accompanying the evaporation of water are sufficient to compress and deform the particles into transparent, void-free film. However, latex films can also be obtained by compression molding of a film of dried latex powder composed of relatively hard polymers, such as polystyrene (PS) or poly (methyl methacrylate) (PMMA) that has T_g above room temperature. Aqueous dispersion of soft latex particles are called low-T, while nonaqueous dispersion of hard polymer particles are generally referred to as high-T. High-T latex particles remain essentially discrete and undeformed during drying. The mechanical properties of such films can be evolved after all the solvent has evaporated by annealing process which first leads to the growth of “necks”, molecularly contacting interfaces between particles and then interdiffusion (equilibration) of material properties within those necks take place.

The process of interparticle polymer interdiffusion has been studied by direct nonradiative energy transfer (DET) using fluorescence decay measurements conjunction with particles labeled with appropriate donor and acceptor chromophors^{1,2,3,4}. This transient fluorescence technique has been used to examine latex film formation of 1 μm diameter high-T (PMMA) particle¹ and of 100 nm diameter low-T poly(butyl methacrylate) (PBMA) particles^{2,3}.

These studies all indicate that in the particular systems examined, annealing the films above T_g leads to polymer interdiffusion at the particle-particle junction as the particle interface heals. Mazur⁵ has written an extensive review on coalescence of polymer particles, in which he mainly discussed the neck growth mechanism and its several geometrical approximations before interdiffusion of polymer chains takes place. Recently, DET and the steady state fluorescence technique have been used in this laboratory to study the interdiffusion processes at the particle-particle junction during film formation by PMMA latex particles⁶⁻⁹.

In this work, latex films formed from P_y labeled high-T latex particles were annealed during equal time intervals at elevated temperatures above T_g and neck growth (void closure process) due to viscous flow was studied by monitoring the direct fluorescence emission intensity (I_{0P}) from a dye using steady state fluorescence (SSF) technique. Equilibration regime was monitored above void closure point using SSF technique by monitoring I_{0P} versus temperature. The evolution in optical clarity is explained by the variation in mean free path ($\langle l \rangle$) of a photon in the latex films at each annealing step. The void closure equation was derived and employed to quantify the temperature dependence of I_{0P} was modeled by assuming the increase in crossing density of chains due to equilibration process. The method developed by Prager and Tirrell¹⁰ was employed to investigate the equilibration process. Activation energies of viscous flow, ΔH and backbone motion,

ΔE were measured and found to be 47 kcal/mol and 44 kcal/mol, respectively during latex film formation.

2. Experimental

Pyrene (P_y)-labeled PMMA polymer particles sterically stabilized by poly(iso butylenes) (PIB) were prepared separately in a two-step process¹¹. Scanning electron microscope studies indicated that these spherical particles ranged in diameter of 1-3 μm . Glass transition temperature of these particles are found to be around 110 $^{\circ}\text{C}$. These particles are made up of polymer with molecular weight of $M_w \approx 1.5 \times 10^5$. A combination of $^1\text{H-NMR}$ and UV analysis indicated that these particles contain 6 mol % PIB and 0.037 mmol P_y groups per gram of polymer (These particles were prepared in Prof. M. A. Winnik Laboratory in Toronto). Latex film preparation was carried out in the following manner. The P_y labeled particles were separately dispersed in heptane in a test tube. After complete mixing, a large drop of the dispersion was dropped on a glass plate with the size of $0.9 \times 3.2 \text{ cm}^2$. The heptane was allowed to evaporate. Then the films were annealed above the glass transition temperature of PMMA for 5, 10, 15, 30 and 60 min. time intervals at temperatures ranging from 110 to 220 $^{\circ}\text{C}$. During annealing, temperature was maintained within $\pm 1 \text{ }^{\circ}\text{C}$.

For steady state fluorescence (SSF) measurements the glass plate was placed in the solid surface accessory of a Perkin-Elmer Model LS-50 fluorescence spectrometer. All measurements were carried out in the front-face position at room temperature. Slit widths were kept at 2.5 mm during all SSF measurements. Pyrene (P_y) was excited at 345 nm and scattered light and fluorescence emission were detected between 360-500 nm range. Film samples were illuminated only during the actual fluorescence measurements and, at all other times, were shielded from the light source. In all experiments maximum peak at 375 nm were used for the P_y intensity (I_{0P}) measurements. The variations in I_{0P} versus temperature are shown in Fig 1a, b, c and d for 10, 15, 30 and 60 min annealing time intervals, respectively.

3. Results and Discussion

As shown in Fig 1, in all fluorescence experiments upon annealing, P_y intensity (I_{0P}) first increased and reached a maximum and then de-

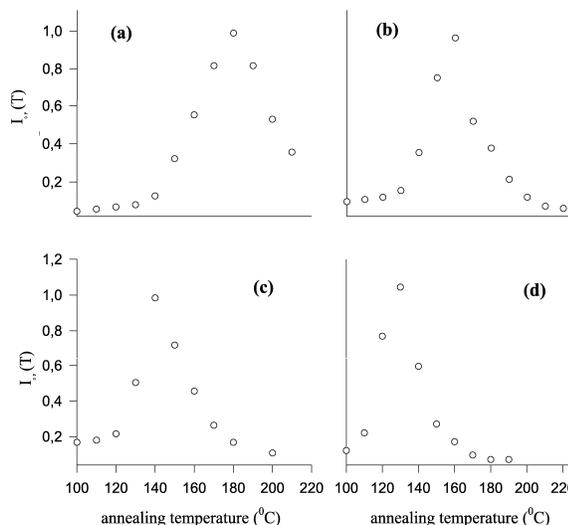


Figure 1. Plot of I_{0P} versus annealing temperature for P_y labeled high-T latex films annealed in a- 10, b- 15, c- 30 and d- 60 min time intervals.

creased. It is well established that the variation in I_{0P} depends on the mean optical path, s , of a photon in the latex films⁶⁻⁹. This mean optical path is directly proportional to the probability of the photon encountering a pyrene molecule. Before annealing, the mean free path ($\langle l \rangle$) is order of the size of the particle and inter-particle voids. After a few steps, the photon reemerges from the front surface of the film. Thus, the mean optical path, s , is very short. After the void closure process is completed, scattering takes place predominantly from the interfaces and the mean free path is of the order of the deformed particle size⁹. In this regime, (with the same number of rescatterings) a photon will stay for a much longer time in the film, and I_{0P} will increase. After the completion of the void closure process, these interfaces are removed by interdiffusion of chains^{7,9}. The film becomes essentially transparent to the photon, the mean free path and s become of the order of the film thickness. As a result I_{0P} decrease.

The maximum in I_{0P} can be explained by the void closure process at the interparticle interface. For instance the time (10 min) can be referred to as the void closure time (t_c) at 180 $^{\circ}\text{C}$, during which polymeric materials occupies the interparticle voids. At this temperature (T_c) and

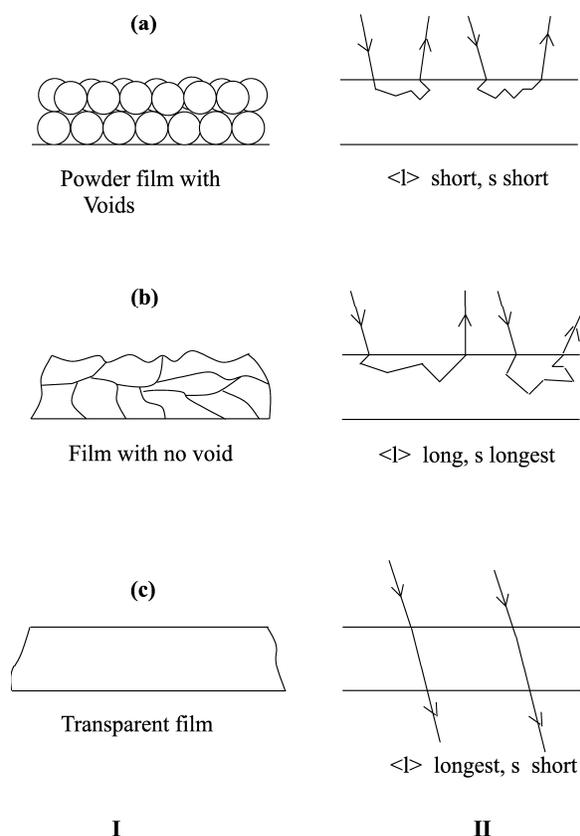


Figure 2. Schematic illustration of the (I) film formation from high-T latex particles (II) variation in mean free and optical paths ($\langle l \rangle$ and s) during film formation; (a), (b) and (c) correspond to the film formation stages explained in the text.

time, (t_c) interparticle voids disappear and the latex film starts to become transparent to the exciting light for P_y molecules. As a result, the emission intensity, I_{0P} reaches a maximum. This point can also be referred to as the healing point (at high temperature) interdiffusion of polymer chains start and equilibration is established upon annealing the latex film. At 210 °C, 90% transparency is reached due to complete equilibration of latex film with the disappearance of all interfaces where I_{0P} is reached its minimum value.

Schematic figures of film formation from high-T latex particles and its relationships with the mean free and optical paths ($\langle l \rangle$) are presented in Fig 2. Early stage of film formation is shown in Fig 2a, where close packed particles form a powder film which includes many voids. This film yields low I_{0P} value due to short $\langle l \rangle$ and s lengths⁷⁻⁹. Fig 2b presents a film where, due to the annealing, interparticle voids start to disappear which gives rise to a higher $\langle l \rangle$ and the longest s values. In such a film one can observe highest I_{0P} intensity. Finally, Fig 2c shows a fully transparent film with the longest $\langle l \rangle$ but shorter s values. This film should present low I_{0P} intensity.

3.1. Voids Closure Mechanism

In the previous section, the maximum in I_{0P} was explained in terms of the void closure process, where polymeric material flows and fills up the interparticle voids. The maximum in each experimental set corresponds to the “void closure time” (t_c) for a given temperature, or the “void closure temperature” (T_c) for the time required for the polymeric material to flow into the voids. For instance, at 140, 160 and 180 °C, t_c values were found to be 30 min, 15 min and 10 min, respectively. At 130 °C the maxima in I_{0P} for the corresponding time intervals does not differ. This may indicate that at this temperature, the void closure times do not change, when the time intervals are increased^{8,9}. In other words, 130 °C is the minimum required temperature for the void closure in high-T latex particles during film formation. For a given t_c and T_c , interparticle voids completely disappear due to viscous flow. As a result, I_{0P} reaches a maximum. These observations can be interpreted by some appropriate models.

Dillon et. al.¹² were the first, postulated that dry sintering of two particles which are in contact with each other occurs through viscous flow of polymer. Particle deformation and void clo-

sure between particles can be induced by shearing stress which is generated by surface tension of polymer i. e. polymer-air interfacial tension. The void closure kinetics can determine the time for optical transparency and latex film formation¹³. An expression to relate the shrinkage of spherical void of radius, r to the viscosity of surrounding medium, η an expression was derived¹⁴.

$$\frac{dr}{dt} = -\frac{\gamma}{2\eta} \left(\frac{1}{\rho(r)} \right) \quad (1)$$

where γ is surface energy, t is time and $\rho(r)$ is the relative density. It has to be noted that here surface energy causes a decrease in void size and the term $\rho(r)$ varies with the microstructural characteristics of the material, such as the number of voids, the initial particle size and packing. Here $\rho(r)$ can be defined as a volume ratio of polymeric material to voids where as r goes to zero $\rho(r)$ increases, however for large r values $\rho(r)$ decreases. Eq 1 is similar to one, which was used to explain the time dependence of the minimum film formation temperature during latex film formation^{15,16}. If the viscosity is constant in time, integration of Eq 1 gives the relation as

$$t = -\frac{2\eta}{\gamma} \int_{r_0}^r \rho(r) dr \quad (2)$$

where r_0 is the initial void radius at time $t=0$.

The dependence of the viscosity of polymer melt on temperature is affected by the overcoming of the forces of macromolecular interaction which enables the segments of polymer chain to jump over from one equilibration position to another. This process happens at temperatures at which free volume becomes large enough and is connected with the overcoming of the potential barrier. The height of this barrier can be characterized by free energy of activation, ΔG during viscous flow. Frenkel-Eyring¹⁷ theory produces the following relation for the temperature dependence of viscosity

$$\eta = \frac{N_0 h}{V} \exp(\Delta/kT) \quad (3)$$

Where N_0 is Avagadro's number, h is Planck's constant, V is molar volume and k is Boltzmann constant. It is known that $\Delta G = \Delta H - T\Delta S$, then Eq 3 can be written as

$$\eta = A \exp(\Delta H/kT) \quad (4)$$

Where ΔH is the activation energy of viscous flow i.e. the amount of heat which must be given to one mole of material for creating the act of a jump during viscous flow. ΔS is the entropy of activation of viscous flow. Here A represents a constant for the related parameters which do not depend on temperature. Combining Eq 2 and 4 the following useful equation is obtained

$$t = -\frac{2A}{\gamma} \exp\left(\frac{\Delta H}{kT}\right) \int_{r_0}^r \rho(r) dr \quad (5)$$

Eq 5 will be employed to interpret the fluorescence data to explained the void closure mechanism in following the sections.

In order to quantify the behavior of I_{0P} below void closure point (T_c, t_c), Eq 5 can be employed by assuming that the interparticle voids are in equal size and number of voids stay constant during film formation (i.e. $\rho(r) \propto r^{-3}$), then integration of Eq 5 gives the relation

$$t = \frac{2AC}{\gamma} \exp\left(\frac{\Delta H}{kT}\right) \left(\frac{1}{r^2} - \frac{1}{r_0^2} \right) \quad (6)$$

Where, C is a constant related to relative density $\rho(r)$. As we stated before, a decrease in void size (r) causes an increase in mean free path $\langle l \rangle$ of a photon, which then results an increase in I_{0P} intensity. This picture can also be visualized by Frenkel's neck formation model¹⁸, which takes into account the identical contacting spheres under the influence of surface tension. Frenkel's model assumes that the displaced volume is redistributed uniformly such that the remaining surfaces keep their spherical shapes but of larger radii, which offers a larger mean free path $\langle l \rangle$ of a photon during its journey in the latex film⁷. If the assumption is made that emission that I_{0P} is inversely proportional to the void radius, r then Eq 6 can be written as

$$t = \frac{2AC}{\gamma} \exp\left(\frac{\Delta H}{kT}\right) I_{op}^2 \quad (7)$$

Here, r_0^{-2} is omitted from the relation since it is very small compared to r^{-2} values after void closure processes start. Eq 7 can be solved for I_{0P} to interpret the results in Fig 1as

$$I_{op}(T) = S(T) \exp\left(-\frac{\Delta H}{2kT}\right) \quad (8)$$

where $S(t)=(\gamma t/2AC)^{1/2}$. For a given time the logarithmic form of Eq 8 can be written as follows

$$\ln I_{op}(T) = \ln S(t) - \frac{\Delta H}{2kT} \quad (9)$$

Below the void closure point (t_c, T_c) data in Fig 1 are fitted to Eq 9 and ΔH values obtained from the slopes of the straight lines in Fig 3. ΔH values are listed in Table I for various time intervals. The averaged ΔH value is found to be 47 kcal/mol which is quite close to the values for carbon chain polymers given in the literature¹⁷. The activation energy of viscous flow i. e. the dependence of viscosity on temperature depend on are determined by the structure of polymer chain. In other words the type of branches and the presence of polar groups in the chain determine the kinetics flexibility of polymer. For carbon chain polymers ΔH are found to be 5 to 7 kcal/mol (polyethylene). ΔH reaches to the value of 15 kcal/mol for poly(iso butylene). For polystyrene whose side groups are phenyl rings ΔH rises to 28 kcal/mol. ΔH is much higher for polyvinyl chloride (35 kcal/mol) and polyvinyl acetate (60 kcal/mol) polymers. Here it has to be noted that curves in Fig 1 are used up to their maxima i. e. left hand side of void closure temperature, T_c Right hand side of the curves in Fig 1 present the interdiffusion process during film formation which will be discussed in the next section.

3.2. Crossing Density and Interdiffusion

When film samples were annealed above the void closure point at elevated temperature in various time intervals, a continuous decrease in I_{0F} intensities were observed. The decrease in I_{0F} was already explained in the previous section, by the increase in transparency of latex film due to disappearing of deformed particle-particle interfaces. As the annealing temperature is increased above T_c some part of polymer chains may cross the junction surface and particle boundaries start to disappear, as a result I_{0F} decrease due to the longer optical path, s of photon.

In order of to quantify these results, the Prager-Tirrell (PT) model¹⁰ for the chain crossing density was employed. The total "crossing density" $\sigma(t)$ (chains per unit area) at junction surface was calculated from the contributions $\sigma_1(t)$ due to chains still retaining some portion of their initial tubes, plus a remainder, $\sigma_2(t)$. Here the $\sigma_2(t)$ contribution comes from chains which have relaxed at least once. In terms of reduced time

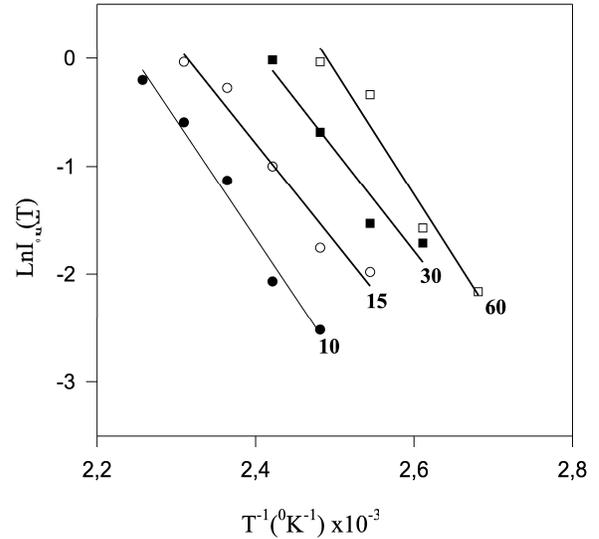


Figure 3. Fit of the data below void closure point in Fig 1 to Eq 9. Slopes of the straight lines produce ΔH values which are listed in Table I. Number on each

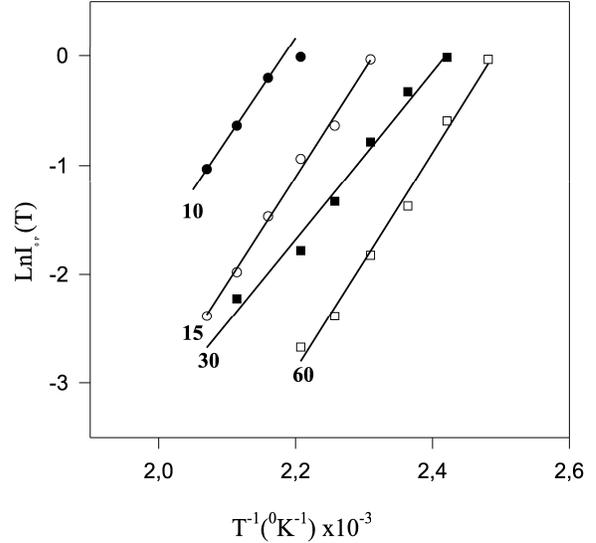


Figure 4. Fit of the data above void closure point in Fig 1 to logarithmic form of Eq 13. Slopes of the straight lines produce ΔE values which are listed in Table I. Number on each curve indicate the annealing time interval in minute.

Table 1

Experimentally measured viscous-flow (ΔH) and back-bone (ΔE) activation energies at various annealing time intervals. Average ΔE values are listed in last column.

Annealing time interval t (min)	5	10	15	30	60	Average
ΔH kcal/mol	57.42	48.35	44.43	39.80	46.00	47.20
ΔE kcal/mol		46.87	49.33	39.60	42.30	44.52

$\tau = 2\nu t/N^2$ the total crossing density can be written as¹⁰

$$\sigma(\tau)/\sigma(\infty) = 2\pi^{-1/2}\tau^{1/2} \quad (10)$$

This was predicted by de Gennes on the basis of scaling arguments. In order to compare our results with the crossing density of the PT model, the temperature dependence of $\sigma(\tau)/\sigma(\infty)$ can be modeled by taking into account the following Arrhenius relation for the linear diffusion coefficient

$$\nu = \nu_0 \exp(-\Delta E/kT) \quad (11)$$

Here ΔE is defined as the activation energy for back and forth motion. Combining Eq 10 and Eq 11 a useful relation is obtained as

$$\sigma(\tau)/\sigma(\infty) = R \exp(-\Delta E/2kT) \quad (12)$$

where $R = (8\nu_0 t/\pi N^2)^{1/2}$ is a temperature independent coefficient.

The decrease in I_{0P} in Fig 1 is already related to the disappearance of particle-particle interface, i. e. as annealing temperature increased, more chains relaxed across the junction surface and as a result the crossing density increases. Now, it can be assumed that I_{0P} is inversely proportional to the crossing density $\sigma(T)$ and then the phenomenological equation can be written as

$$I_{op}(T)/I_{op}(\infty) = R \exp(\Delta E/2kT) \quad (13)$$

Logarithmic plots of I_{0P} vs T^{-1} are presented in Fig 4 for 60, 30, 15 and 10 min annealing time intervals, respectively. The activation energies, ΔE are produced by fitting the data in Fig 4 to Eq 13 and are listed in Table I. The averaged value is found to be 44 kcal/mol, which is slightly larger than the backbone activation energies measured in our previous works^{1,7,9}. It is well known that backbone activation energy is responsibly from the motion of center of mass of a chain. Here it is reasonable to accept that σ_2

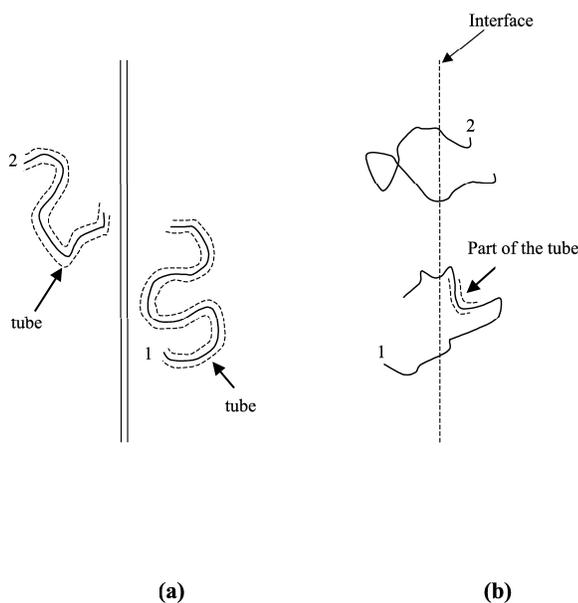


Figure 5. Representation of the interdiffusion processes.

term of crossing density contributes to the disappearance of interfaces during latex film formation. In other words, chains which have relaxed at least once are responsible from the disappearance of particle-particle boundaries. Fig 5 shows a diagram of the contribution of σ_1 and σ_2 terms for the disappearance of particle-particle boundary. Here it has to be noted that according PT model σ_2 contribution dominated at long times, which is consistent with our measurement i. e. polymer interdiffusion starts above (t_c, T_c) point after the complete wetting is reached. Here one may argue that, since longer polymer chains need larger activation energy to perform their interdiffusion, the measured ΔE (44 kcal/mol) value should be larger than the previously measured ΔE (30 kcal/mol) values which were obtained in wider temperature range^{7,9}. Here it is interesting to note that I_{0P} intensity gives the information on both void-closure and interdiffusion processes.

4. Acknowledgements

We would like to thank Prof. M. A. Winnik for supplying us with the latex particles.

References

- [1] Ö. Pekcan, M. A. Winnik, and M. D. Croucher, *Macromolecules* **23**, 2673 (1990).
- [2] C. L. Zhao, Y. Wang, Z. Hruska, and M. A. Winnik, *Macromolecules* **23**, 4082 (1990).
- [3] Y. Wang, C. L. Zhao, and M. A. Winnik, *J. Chem. Phys.* **95**, 2143 (1991).
- [4] E. M. Boczar, B. C. Dionne, Z. Fu, A. B. Kirk, P. M. Lesko, and A. D. Koller, *Macromolecules* **26**, 5772 (1993).
- [5] S. Mazur, *Coalescence of Polymer Particles* (Polymer Powder Technology, Eds. M. Maukis and V. Rosenweig, John Wiley and Sons 1996).
- [6] Ö. Pekcan and M. Canpolat, *J. Appl. Polym. Sci.* **59**, 277 (1996).
- [7] M. Canpolat and Ö. Pekcan, *Polymer* **36**, 4433 (1995).
- [8] Ö. Pekcan, *Trends in Polymer Science* **2**, 236 (1994).
- [9] M. Canpolat and Ö. Pekcan, *Polymer* **36**, 2025 (1995).
- [10] S. Prager and M. Tirrell, *J. Chem. Phys.* **75**, 5194 (1981).
- [11] Ö. Pekcan, M. A. Pekcan, and L. Egan, *Macromolecules* **16**, 702 (1983).
- [12] R. E. Dillon, L. A. Matheson, and E. B. Bradford, *J. Colloid Sci.* **6**, 108 (1951).
- [13] J. L. Keddie, P. Meredith, R.A.L Jones, and A.M. Donald (Proc. ACS., Chicago 1995).
- [14] J. K. Mackenzie and R. Shuttleworth, *Proc. Phys. Soc.* **62**, 838 (1949).
- [15] P. R. Sperry, B. S. Snyder, M. L. O'Dowd, and P. M. Lesko, *Langmuir* **10**, 2619 (1994).
- [16] G.B. Mc Kenna,., In *Comprehensive Polymer Science*, Vol. 2 (C. Booth and C. Price, (Eds.), Pergamon Press, Oxford UK., 1989).
- [17] A. Tager, *Physical Chemistry of Polymers* (MIR Publisher Moscow 1978).
- [18] J. Frenkel, *J. Phys. USSR* **9**, 385 (1945).