Poly(ethylene oxide)/Poly(styrene-co-acrylic acid) Blends의 등온 결정화 속도에 관한 연구

이상철*, 이무성, 조원호

서울대학교 섬유공학과, *금오공과대학 고분자공학과

Kinetics of Isothermal Crystallization in Poly(ethylene oxide) and Poly(styrene-co-acrylic acid)Blends

Sang Cheol Lèe*, Moo Sung Lee, and Won Ho Jo

Departmemt of Textile Engineering, Seoul National University, Seoul, 151-742

**Department of Polymer Sience and Engineering, Kum-Oh National Institute of*

Technology, Kumi, Kyung Buk, 730-070

요   약   시차주사 열분석기를 이용하여 poly(ethylene oxide)(PEO)/poly(styrene-co-acrylic acid)
(SAA) blends에 대한 등온 결정화 속도를 blend의 조성, 사용한 SAA의 공중합조성 및 결정화 온도
에 따라 조사하였다. 실험결과는 Avrami 방정식을 이용하여 분석하였다. Avrami지수는 결정화 온도
에 관계없이 거의 모든 blend 시료에서 2의 값을 나타내었다. 결정화 속도는 blend시료의 SAA 함량
및 사용한 SAA 공중합체의 아크릴산함량이 증가함에 따라 급격히 느려졌다.

Abstract The kinetics of isothermal crystallization in blends of poly(ethylene oxide)(PEO) and poly
(styrene-co-acrylic acid) (SAA) has been examined as a function of the blend ratio, the copolymer
composition, and the crystallization temperature, based on the Avrami equation. The Avrami exponents
were mostly close to 2, independent of the crystallization temperature. The crystallization rate of PEO in
PEO/SAA blends decreased with the increase of SAA content. And also, the higher the acrylic acid con-
tent in the SAA copolymer, the slower the crystallization rate of PEO in the blends.

INTRODUCTION

The study of the crystallization behavior in polymer blends may be useful way to obtain fundamental information about miscibility of polymer pairs.[1] The crystallization rate of a crystalline polymer in the blend system can be influenced by the addition of a miscible amorphous polymer.[2-8] On the other hand, the added polymer does not affect the crystallization of the crystalline polymer if the polymer pair is immiscible.

In our previous work,[9] we reported that poly(ethylene oxide) (PEO) is miscible with poly(styrene-co-acrylic acid) (SAA) having acrylic acid content greater than 7 mole % and that both the hydrogen bonding between ethylene oxide and acrylic acid segments and the intramolecular repulsive force in SAA co-polymers are responsible for the miscibility.

In this work, isothermal crystallization kinet- ics for the blends of PEO and SAA was stud- ied by differential scanning calorimetry to ex- amine the influence of copolymer composition and blend ratio on the crystallization rate.

EXPERIMENTAL

PEO($M_w = 1.0 \times 10^5$, $T_g = -56°C$, equilibrium

Table 1. Properties of SAA copolymers

Sample	Copolymer Composition, mole % of acrylic acid	Intrinsic Viscosity, dL/g	T_g, °C
SAA7	7.0	1.24	108
SAA15	15.0	1.19	115
SAA19	19.0	1.08	119
SAA29	29.0	0.93	125

melting point $=68.7$°C) was obtained from Al-drich Co. The experimental methods of synthesis of SAA copolymers, characterization of the copolymers, and preparation of blends were specified in a previous paper.[3] The copolymer composition and other properties are listed in table 1.

The crystallization rate was measured by Du Pont 910 differential scanning calorimeter (DSC) equipped with a mechanical cooling accessory. Samples were first melted at 85°C for 5 min, then quickly cooled to the crystallization temperature(T_c) and kept at T_c for at least 20 min, recording the heat of crystallization as a function of time at T_c. The weight fraction X_t of material crystallized after time t was determined by the relation[10, 11].

$$X_t = \int_0^t (dH/dt)dt \Big/ \int_0^\infty (dH/dt)dt \qquad (1)$$

where the first integral is the heat generated at time t and the second is the total heat of crystallization for $t=\infty$. X_t can be obtained from DSC crystallization thermogram.

RESULTS AND DISCUSSION

The crystallization isotherms were analyzed with the Avrami equation[12]:

$$1 - X_t = \exp(-Kt^n) \qquad (2)$$

where K is the overall kinetic rate constant which depends on the rate of nucleation and growth, and n, so called Avrami exponent, is a parameter that depends on the nature of the primary nucleation and the geometry of growing crystals. Eq(2) can be transformed into

$$\log[-\ln(1-X_t)] = n \log t + \log K \qquad (3)$$

The values of K and n can be obtained for each isothermal crystallization temperature from the intercept and the slope of a straight line obtained by using the relation:

$$K = \ln 2/t_{1/2}^n \qquad (4)$$

where $t_{1/2}$, the half–crystallization time, is defined as the time for half of the crystallinity to develop, which can be determined from the crystallization isotherm.

Figure 1 shows the Avrami plots for PEO/SAA7(85/15) blend at various crystallization temperatures. The linear relationships between $\log[-\ln(1-X_t)]$ and $\log t$ for a large part of crystallization process indicate that the crystallization kinetics of this blend follows the
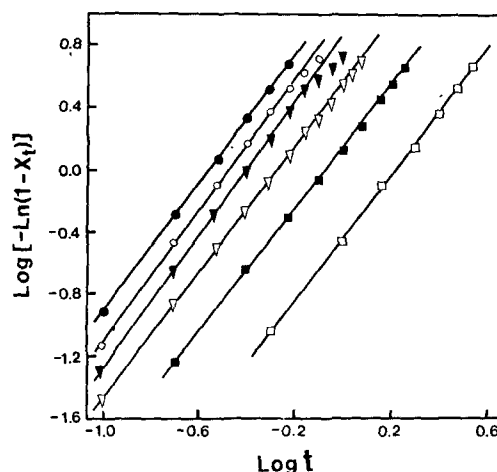

Fig. 1. Avrami plots for PEO/SAA7(85/15, wt/wt) blend at various crystallization temperatures : (●) 36.1°C, (○) 37.9°C, (▼) 39.8°C, (▽) 41.8°C, (■) 43.7°C, and (□) 45.6°C.

Table 2. Kinetic data of the isothermal crystallization for PEO/SAA15 blends

PEO/SAA15(wt/wt)	T_c, °C	n	K, min^{-n}	$t_{1/2}$, min
85/15	34.1	2.08	6.39	0.34
	36.1	1.96	4.75	0.37
	38.0	1.92	2.88	0.48
	39.7	1.92	1.27	0.73
	41.7	2.01	0.49	1.19
	43.7	1.96	0.15	2.19
80/20	31.3	2.23	5.70	0.39
	33.3	2.05	3.16	0.48
	35.1	2.04	1.82	0.62
	37.0	2.07	1.17	0.78
	38.9	2.08	0.28	1.55
	41.0	2.16	0.07	2.90
75/25	31.3	2.31	0.42	1.24
	32.9	2.44	0.16	1.85
	35.0	2.14	0.11	2.36
	36.9	1.86	0.12	2.55
	38.8	1.97	0.04	4.11
	40.6	1.63	0.04	5.76
70/30	31.3	1.44	0.13	3.20
	33.3	1.62	0.06	4.74
	35.1	1.77	0.01	9.67

Table 3. Kinetic data of the iosthermal crystallization for PEO/SAA(85/15) blends

| Sample	T_c, °C	n	K, min^{-n}	$t_{1/2}$, min
PEO/SAA7	36.1	2.04	13.52	0.23
	37.9	2.04	8.83	0.29
	39.8	2.04	6.16	0.34
	41.8	1.98	3.30	0.46
	43.7	1.99	1.38	0.71
	45.6	2.00	0.36	1.39
PEO/SAA15	34.1	2.08	6.39	0.34
	36.1	1.96	4.75	0.37
	38.0	1.92	2.88	0.48
	39.7	1.92	1.27	0.73
	41.7	2.01	0.49	1.19
	43.7	1.96	0.15	2.19
PEO/SAA19	33.0	1.98	2.06	0.58
	34.9	2.01	1.08	0.80
	36.8	1.99	0.43	1.28
	38.7	2.04	0.15	2.09
	40.6	2.06	0.03	4.42
PEO/SAA29	32.1	2.11	1.15	0.79
	34.0	1.96	0.68	1.00
	35.9	2.04	0.30	1.52
	37.8	2.10	0.13	2.19
	39.7	1.82	0.06	3.77
	41.6	1.75	0.01	9.88
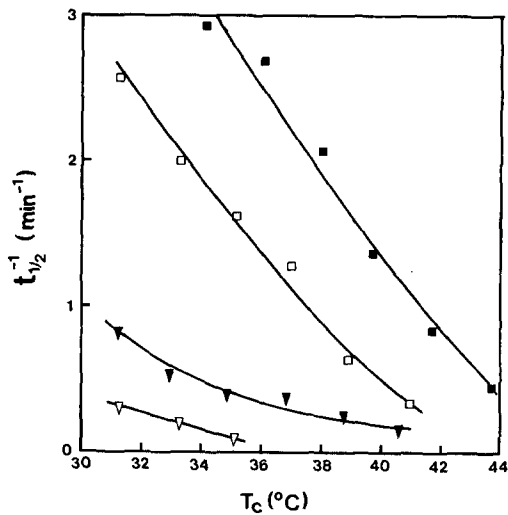
Fig. 2. Reciprocal of crystallization half—time vs. crystallization temperature for PEO/SAA15 blends : (■) 85, (□) 80, (▼) 75, and (▽) 70 weight percent PEO.

Fig. 3. Reciprocal of crystallization half—time vs. crystallization temperature for PEO/SAA (85/15) blends:(■) SAA7, (□) SAA15, (▼) SAA19, and (▽) SAA29.

Avrami equation up to high degree of conversion. The other blends also show similar behavior.

The kinetic parameters are listed in table 2 for PEO/SAA15 blends of various blend ratio, and those are listed in table 3 for the blends with the fixed blend ratio (85/15) of various copolymer compositions of SAA used. The Avrami exponents are independent of the crystallization temperature and these values are close to 2 for all the samples except for PEO/SAA15 (70/30) blends. It means that the crystallizaion mechanisms for these blends are similar, while the crystallization process for PEO/SAA15 (70/30) blend differs from the above cases.

As shown in figure 2, the isothermal crystallization rate represented by $t_{1/2}^{-1}$ decreases with increasing the crystallization temperature and decreases with the addition of non—crystallizable SAA component. According to the general theory for the growth rate of a miscible blend consisting of a crystalline and an amorphous polymer the glass transition temperature of the blend significantly influenc-
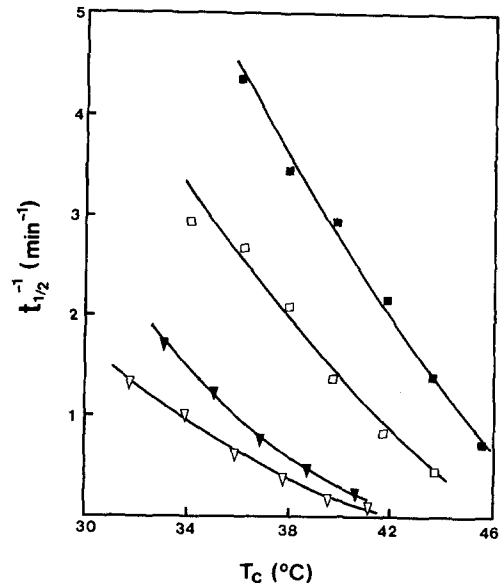
es the crystallization rate of the crystalline component.[13] The addition of an amorphous polymer to a crystallizable one will lower the crystallization rate if the glass transition temperature of the blend is higher than that of the crystalline one, since the transport of the crystallizable polymer onto the crystal growth surface is retarded. Conversely, a higher crystallization rate will be expected if the glass transition temperature of the blend is lower than that of the crystallizable one. In this study, the glass transition temperatures of the blends are higher than that of pure PEO.[9] Therefore, the diffusion of PEO to the crystal growth sites becomes difficult and the crystallization rate decreases.

In order to investigate the effect of the copolymer composition on the isothermal crystallization rate, the $t_{1/2}^{-1}$ is plotted against T_c for the fixed composition blend samples using the different copolymer compositions in figure 3. This plot indicates that, at constant T_c, the crystallization rate of the blends decreases

with increasing the acrylic acid (AA) content of the copolymer. The glass transition temperature increases as the AA content in the SAA copolymers increases, since the strength of intermolecular interaction between PEO and SAA increases with the AA content in the SAA copolymers. Therefore, the segmental motion is more restricted with increasing the AA content in the SAA copolymers, which leads to the decrease of the crystallization rate of the blends.

CONCLUSIONS

The crystallization kinetics for PEO/SAA blends was investigated on the basis of the Avrami equation. The crystallization process of these blends follows the Avrami equation up to high degree of conversion. The Avrami exponents are independent of the crystallization temperature and these values are close to 2 for all the samples except for PEO/SAA15 (70/30) blend.

The isothermal crystallization rate of PEO in PEO/SAA blends decreases with increasing the SAA content and with increasing the acrylic acid content in the SAA copolymers at the fixed blend ratio. This result is well consistent with the facts that these blends are miscible and that the interaction energy density increases with the acrylic acid content in the SAA copolymers.[9]

REFERENCES

1. O. Olabisi, L.M. Robeson, and M.T. Shaw, Polymer-Polymer Miscibility, Academic Press, New York, 1979
2. M.L. Addonizio, E. Martuscelli, and C. Silvestre, Polymer, **28**, 183(1987)
3. T.T. Wang and T. Nishi, Macromolecules, **10**, 421(1977)
4. E. Calahorra, M. Cortazar, and G.M. Guzman, Polym. Commun., **24**, 211(1983)
5. G.C. Alfonso and T.P.Russell, Macromolecules, **19**, 1143(1986)
6. E. Matuscelli, M. Pracella, and Wang Ping Yue, Polymer, **25**, 1097(1984)
7. Issa A. Katime, M.S. Anasagasti, M.C. Peleteiro, and R. Valenciano, Eur. Polym. J., **23**, 907(1987)
8. E. Martuscelli. Polym. Eng. Sci., **24**, 563 (1984)
9. W.H. Jo and S.C. Lee, Macromolecules, **23**, 2261(1990)
10. A. Booth and J.N. Hay, Polymer, **10**, 95 (1964)
11. J. N. Hay, P.P. Fitzgerald, and M. Wiles, Polymer, **17**, 1015(1976)
12. M. Avrami, J. Chem. Phys., **7**, 1103 (1939); **8**, 212(1940); **9**, 177(1941)
13. F. Gornish and J.D. Hoffman, in Nucleation Phenomena, A.S. Michaels, Ed., **53**, Am. Chem. Soc., Washington D.C., 1966