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Copolymerization and Characteristics of Styrene and Fluorine-Containing Acrylate

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(perfluoro group : $CF_3(CF_2)_nCH_2CH_2-$; $n=5, 7, 9, 11$) perfluoroalkylethyl acrylate(FA) styrene bulk 60
AIBN 10%
Kelen - Tüdös r_1
 r_2 FT - IR 1H - NMR
 1H - NMR DSC TGA
가 가 PMMA

ABSTRACT : The free radical bulk copolymerizations of perfluoroalkylethyl acrylate(FA) containing perfluoro group ($CF_3(CF_2)_nCH_2CH_2$; $n = 5, 7, 9, 11$) with styrene were conducted at 60 using AIBN as an initiator. Reactivity ratios(r_1, r_2) were determined from monomer feed compositions and the NMR spectroscopically measured copolymer compositions using Kelen - Tüdös method. The structures of copolymers were characterized with FT - IR and 1H - NMR analysis. Their thermal properties investigated with DSC and TGA were decreased with increasing the content of fluorinated acrylate in the copolymer. Their surface free energies were calculated with measuring contact angles of the copolymers and PMMA blends with a small amount of them.

Keywords : perfluoroalkyl acrylate, radical copolymerization, monomer reactivity ratio, contact angle, surface free energy.

1,2

C - F

C - C packing

5 10 dyne/cm

3-6

가

가

가

가

가

7-10

per -

fluoroalkyl ethyl acrylate(FA)

(DSC)

(TGA)

가 가 PMMA

FA (Hoechst Co : Fluowet AC - 800) 가 8 95%

Styrene (Kanto Chemical Co., Japan) 10% NaOH solution

3 4

Hayashi Pure Chemical 2, 2' - azobisisobutyronitrile(AIBN)

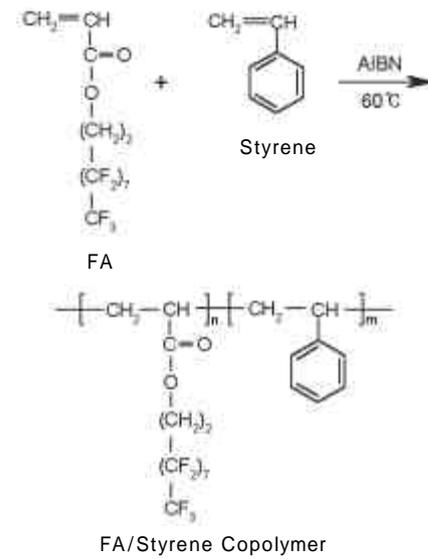


Figure 1. The reaction scheme of FA/styrene copolymerization.

FA styrene 1/9,
2/8, 3/7, 4/6, 5/5, 6/4, 7/3, 8/2, 9/1

0.2 wt% AIBN

oil bath

(60) bulk

10%

scheme Figure 1

PMMA

/PMMA

THF

FT - IR ¹H - NMR
 BIO - RAD EXCALIBUR
 Series FTS - 3000 spectrophotometer
 resolution 4 cm⁻¹ 32 scan trans -
 mittance spectra ¹H - NMR
 Aldrich tetrahydrofuran - d₈ (99.5%)
 BRUKER AMX 300 MHz ¹H -
 NMR spectrometer
 styrene FA
 eluent
 THF, column Shodex KF series column
 Waters GPC
 40 flow rate 1.0 mL/min
 refractive index (RI) detector
 Mettler Toledo
 DSC 821e model
 10 mg
 crucible 100 cm³/min
 - 50 200 10 /min
 가
 crucible 6 10 mg
 40 500
 20 /min Mettler Toledo TGA - 50
 가 (: 22)
 goniometer (Rame - Hart inc., 100 -
 series)
 drop
 가 2 3

FA styrene
 1/9, 2/8, 3/7, 4/6, 5/5, 6/4, 7/3, 8/2, 9/1
 FA 가
 10%
 가 가 10%
 Styrene
 가
 FA 가 가
 가
 가
 FA styrene 1/9
 9/1 2 가
 가
 Figure 2 FA styrene FA
 styrene FT - IR
 FA 1740 cm⁻¹

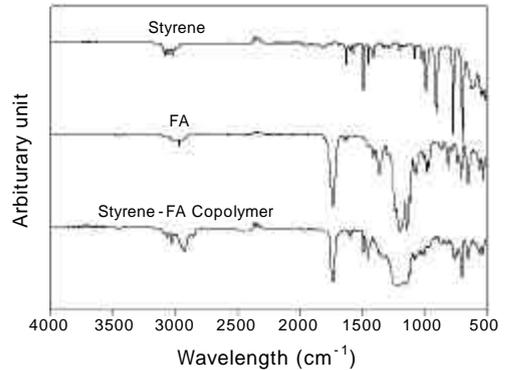


Figure 2. FT - IR spectra of FA, styrene monomer and FA/styrene (6/4) copolymer.

(C=O) 가
 1100 1300 cm⁻¹ C-F 가
 styrene 1430 1665 cm⁻¹ aromatic 가
 C=C 가
 2800 2900 cm⁻¹ C-H aliphatic 가
 (CH₂, CH₃) 가
 Styrene 1430 1665 cm⁻¹ 가
 2800 2900 cm⁻¹ 가
 가 FA 가
 1100 1300 cm⁻¹ 1740 cm⁻¹ 가
 styrene 가
 가

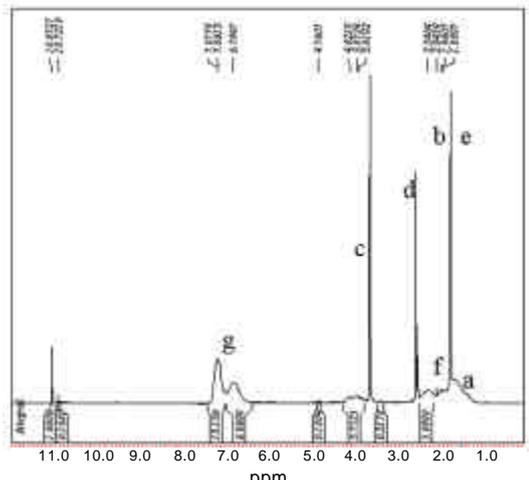
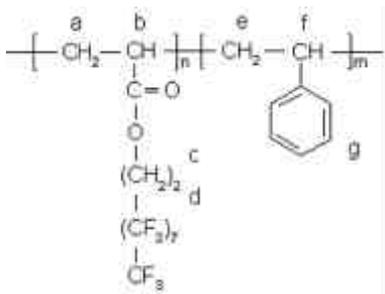


Figure 3. ¹H-NMR spectrum of FA/styrene(3/7) copolymer.

Table 1. Copolymer Composition as a Function of Monomer Composition for the FA(M₁)/Styrene(M₂)

| monomer composition (f ₁) | reaction time(min) | conversion(%) | copolymer composition (F ₁) |
|---------------------------------------|--------------------|---------------|---|
| 0.1 | 90 | 10.1 | 0.30 |
| 0.2 | 95 | 8.4 | 0.47 |
| 0.3 | 100 | 5.2 | 0.58 |
| 0.4 | 110 | 9.4 | 0.80 |
| 0.5 | 150 | 10.5 | 0.89 |
| 0.6 | 170 | 11.2 | 0.92 |
| 0.7 | 190 | 6.1 | 0.91 |
| 0.8 | 200 | 10.5 | 0.95 |
| 0.9 | 210 | 10.2 | 0.97 |

f₁ : mole fraction of FA in the comonomers.
 F₁ : mole fraction of FA in the copolymers.

Table 2. Molecular Weight of FA/Styrene Copolymers by GPC

| mole fraction of FA(M ₁) in feed | GPC | | |
|--|----------------|----------------|---------------------------------------|
| | M _n | M _w | PDI (M _w /M _n) |
| 0.10 | 67435 | 97302 | 1.443 |
| 0.20 | 68688 | 102645 | 1.494 |
| 0.30 | 60079 | 109691 | 1.826 |

¹H-NMR Figure 3
 FA styrene ¹H-NMR
 styrene aromatic proton 7.0 ppm
 methylene group
 proton 1.7 1.8 ppm 2.1 ppm
 FA OCH₂- proton
 3.5 3.6 ppm -CH₂(CF₂)₇CF₃
 proton 2.4 2.6 ppm
 methylene group proton
 1.5 1.8 ppm ¹H-NMR
 가
¹H-NMR
 Table 1

(GPC)
 Table 2

Table 1

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \quad (1)$$

$$\frac{d[M_1]/d[M_2]}{[M_1]/[M_2]} = \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}$$

$$r_1 = k_{11}/k_{12}, \quad r_2 = k_{22}/k_{21}$$

$k_{11}, k_{12}, k_{21}, k_{22}$

r_1, r_2

1975 (1)

20%

$$h = (r_1 + r_2/a)\xi - r_2/a \quad (2)$$

$$h = G/(a+F)$$

$$\xi = F/(a+F), \quad F = X^2/Y, \quad G = X(Y-1)/Y, \quad a = \sqrt{F_{\min} \times F_{\max}}$$

$X = M_1/M_2, \quad Y = m_1/m_2, \quad M_1, M_2$

m_1, m_2

$$(2) \quad h = r_2/a, \quad \xi = 1, \quad h = r_1$$

$$h = r_2/a, \quad \xi = 1, \quad h = r_1$$

Figure 4 FA

FA

Kelen-Tod s

Table 3

h, ξ

Figure 5

$$(4.7) \quad (-0.4467)$$

(2)

$r_2(\text{styrene})$

4.25, $r_2 = 0.12$

FA가 styrene

styrene

FA

r_1, r_2

가

가

Table 3. Determination of Monomer Reactivity Ratio for FA/Styrene Copolymer Systems

| X^a | Y^b | F^c | G^d | ϵ^e | $=F/(a+F)$ | $=G/(a+F)$ |
|-------|-------|--------|---------|--------------|------------|------------|
| 0.11 | 0.43 | 0.0288 | -0.1482 | | 0.0968 | -0.4981 |
| 0.25 | 0.90 | 0.0696 | -0.0285 | | 0.2059 | -0.0844 |
| 0.43 | 1.40 | 0.1308 | 0.1233 | | 0.3275 | 0.3086 |
| 0.67 | 4.00 | 0.1111 | 0.5000 | | 0.2926 | 1.3167 |
| 1.00 | 8.10 | 0.1236 | 0.8764 | 0.2686 | 0.3151 | 2.2344 |
| 1.50 | 9.00 | 0.2500 | 1.3333 | | 0.4820 | 2.5708 |
| 2.33 | 10.11 | 0.5385 | 2.1026 | | 0.6672 | 2.6051 |
| 4.00 | 19.00 | 0.8421 | 3.7895 | | 0.7581 | 3.4117 |
| 9.00 | 32.33 | 2.5051 | 8.7217 | | 0.9032 | 3.1443 |

^a $X = M_1/M_2$, ^b $Y = m_1/m_2$, ^c $F = X^2/Y$, ^d $G = X(Y-1)/Y$.

^e $\epsilon = \sqrt{F_{\min} \times F_{\max}}$.

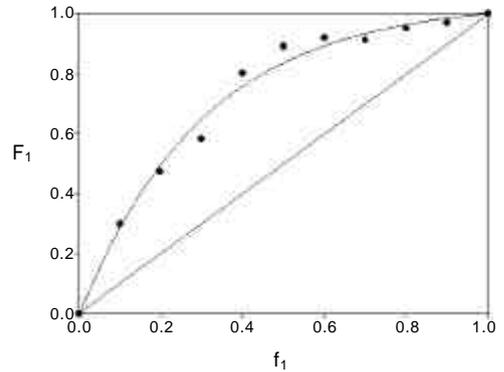


Figure 4. Monomer-copolymer composition curve in the copolymerization of FA with styrene at 60.

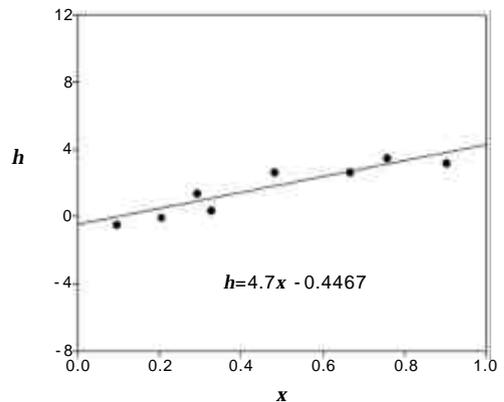


Figure 5. Reactivity ratios of FA/styrene copolymer systems.

FA

polystyrene

DSC thermogram Figure 6 (a)

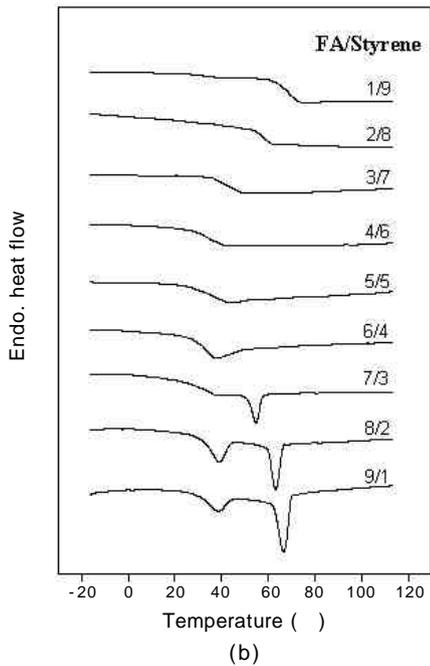
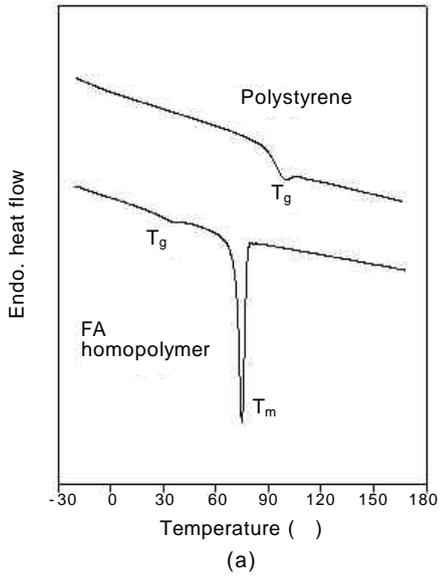


Figure 6. DSC thermograms of (a) FA homopolymer and polystyrene and (b) FA/styrene copolymers.

가 polystyrene T_g
FA T_m

DSC thermogram Figure 6 (b) 100%

Figure 4
styrene T_g가
T_g가 100 polystyrene
FA 4/6
38 5/5 9/1
T_g 38 39
FA
가 double
layer 가
single layer

Figure 6 DSC thermogram
FA 가
FA
thermogram Figure 7 TGA
FA TGA
Table 4
가
12 9/1 150

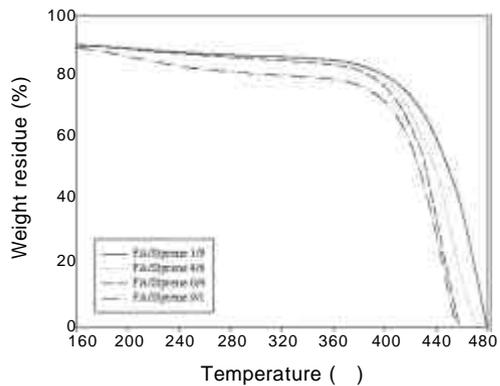


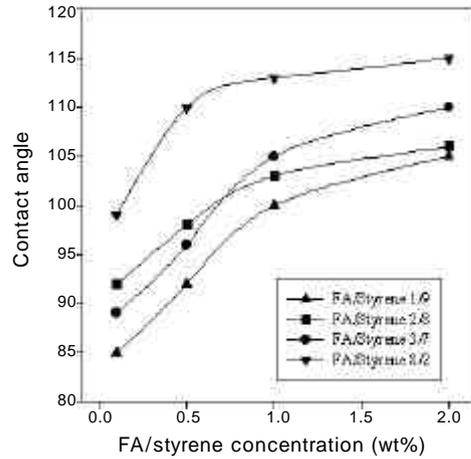
Figure 7. TGA thermograms of FA/styrene copolymers.

Table 4. TGA Results of FA/Styrene Copolymers

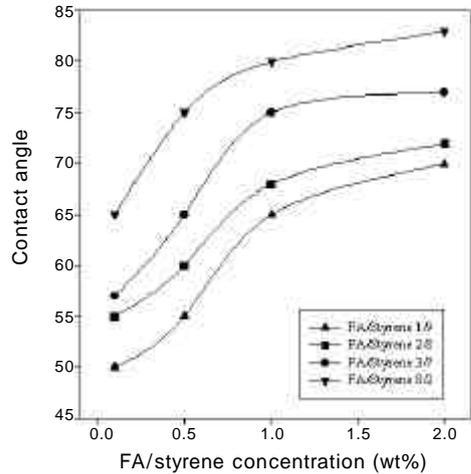
| monomer mole ratio | copolymer FA composition | 5% weight loss temperature() | degradation temperature() |
|--------------------|--------------------------|-------------------------------|----------------------------|
| polystyrene | 0.00 | 386.05 | 441.00 |
| 1/9 | 0.30 | 382.17 | 436.80 |
| 2/8 | 0.47 | 383.23 | 427.34 |
| 3/7 | 0.58 | 380.82 | 426.51 |
| 4/6 | 0.80 | 330.67 | 425.25 |
| 5/5 | 0.89 | 321.15 | 424.96 |
| 6/4 | 0.92 | 316.91 | 418.95 |
| 7/3 | 0.91 | 363.00 | 421.16 |
| 8/2 | 0.95 | 342.15 | 417.52 |
| 9/1 | 0.97 | 250.75 | 413.20 |
| FA homopolymer | 1.00 | 363.42 | 402.49 |

Table 5. Inherent Contact Angles and Surface Free Energy of PMMA and FA/Styrene Copolymers

| PMMA and FA/styrene copolymers | copolymer FA composition | contact angles | | surface free energy (dyne/cm) |
|--------------------------------|--------------------------|----------------|-----------|-------------------------------|
| | | water (deg.) | MI (deg.) | |
| PMMA | - | 75 | 45 | 40.013 |
| FA/styrene (1 : 9) | 0.30 | 105 | 74 | 20.718 |
| FA/styrene (2 : 8) | 0.47 | 108 | 75 | 20.164 |
| FA/styrene (3 : 7) | 0.58 | 112 | 78 | 18.654 |
| FA/styrene (8 : 2) | 0.95 | 116 | 85 | 15.119 |



(a)



(b)

Figure 8. Contact angles of (a) water and (b) MI for copolymer/PMMA blends.

가 400
 . 9/1
 400 . Degradation point
 FA
 . /PMMA
 가 FA
 . Polystyrene
 FA
 goniometer
 MI
 (LV^d)
 PMMA
 Table 5
 Table 4

가 FA
 . Polystyrene
 FA
 37 dyne/cm
 10 dyne/cm
 Table 5
 PMMA

Figure 9(a)

FA 가

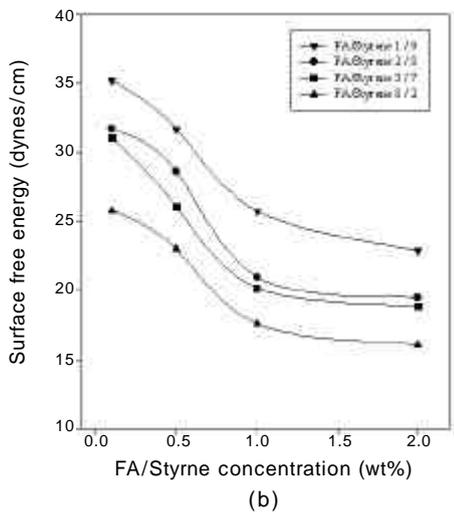
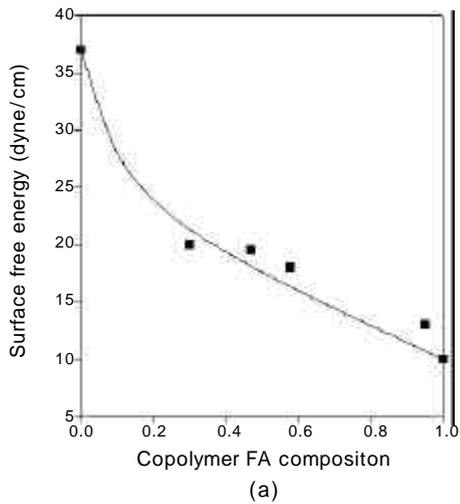


Figure 9. Surface free energy of (a) FA/styrene copolymers with variable FA composition and (b) copolymer/PMMA blends.

PMMA (0.1, 0.5, 1.0, 2.0 wt%)
 MI 가 가 MI
 Figure 8(a) 8(b)

Figure 9(b) FA 가 MI

가 0.1 2.0 wt% 가
 가 가
 가 1.0 wt% 가
 가 0.1, 0.5 wt% 가 1.0 wt% 가 1.0 wt% 가
 가 1.0 wt% 가
 가 40 dyne/cm 가 PMMA 가
 1. FT - IR ¹H - NMR
¹H - NMR Kelen -
 T d s , r₁, r₂ 4.25,
 0.12
 2. 가 1/9 4/6 styrene T_g가 T_g
 가 5/5 9/1

FA 가
 3. MI (LV^d) (LV^D)
 20 dyne/cm
 0.1, 0.5, 1.0, 2.0 wt% 40 dyne/cm
 PMMA 가

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