

# Free Radical Co- and Terpolymerization of Styrene, Hydrogenated Cardanyl Acrylate, and Cardanyl Acetate

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**ABSTRACT:** Hydrogenated cardanyl acrylate (HCA) and cardanyl acetate (CACE) were synthesized from cardanol. The copolymerizations of HCA, CACE, and styrene (S) with methyl ethyl ketone peroxide (MEKP) and cobalt salt as the initiator were studied by FTIR. Based on FTIR results the reactivity ratios of the three copolymerization systems S-HCA, S-CACE, and HCA-CACE were determined by three different methods (Mayo-Lewis, Fineman-Ross, and

Kelen-Tüdös). Results obtained from the three methods are in good agreement. Instantaneous compositions and composition shift as a function of conversion is calculated for the S-HCA-CACE system with different feed compositions. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 1399–1409, 2003

**Key words:** copolymerization; FTIR; kinetics; cardanyl

## INTRODUCTION

Previous work<sup>1–3</sup> describes the synthesis and characterization of cardanyl acrylate (CA) (Scheme 1) with two kinds of double bonds, namely the acrylic group and the double bonds in the long alkyl side chain (C<sub>15</sub>) from cardanol. Several studies<sup>2,3</sup> have been done to clarify the reaction between CA and styrene. However, up to now kinetic investigations of CA in free radical (co)polymerization reactions have not been carried out.

The determination of reactivity ratios for copolymerization between CA and styrene (S) is the aim of this study. To reduce the complexity of the CA-Styrene system, and to be able to understand the reactivity of each kind of double bond individually, the model compounds such as hydrogenated cardanyl acrylate [HCA contains only the acrylic double bond (= acry)] and cardanyl acetate [CACE contains only alkyl side chain double bonds (= car)s] were synthesized.

Calculations of the reactivity ratios of the copolymerization of double bonds of the acrylic moiety and the side chain in HCA and CACE, respectively, with

styrene double bonds are determined, and will be helpful to understand the characteristics of the complex radical terpolymerization of CA and styrene.

The three methods by Mayo-Lewis,<sup>5</sup> Fineman-Ross,<sup>6</sup> and Kelen-Tüdös<sup>7,8</sup> were used to determine the reactivity ratios. The reactivity ratio data was obtained by FTIR measurements.

## Estimation of monomer reactivity ratios

The relationship between the feed monomer composition and the instantaneous composition of copolymer is given by the well-known copolymerization equation:<sup>4</sup>

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

where [M<sub>1</sub>] and [M<sub>2</sub>] are the concentrations of monomers M<sub>1</sub> and M<sub>2</sub> in the feed.

$d[M_1]$  and  $d[M_2]$  are the amount of monomer M<sub>1</sub> and that of monomer M<sub>2</sub> that have been converted into copolymer during a time interval  $dt$ , respectively.

$r_1, r_2$  are reactivity ratios;  $r_1 = k_{11}/k_{12}$  and  $r_2 = k_{22}/k_{21}$ .

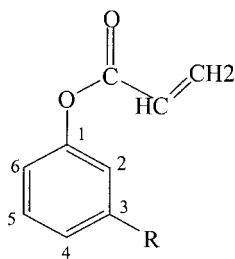
## MAYO-LEWIS METHOD<sup>5</sup>

According to Mayo-Lewis, eq. (2) can be obtained from eq. (1):

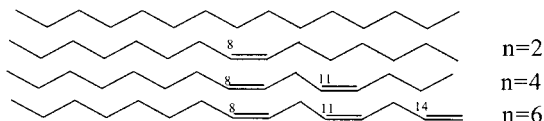
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where  $R = C_{15}H_{31-n}$ , which is a composition of differently unsaturated components as follows:



**Scheme 1** The chemical structure of cardanyl acrylate.

$$r_2 = \frac{\log \frac{[M_2]_0}{[M_2]} - \frac{1}{p} \log \frac{1-p \frac{[M_1]}{[M_2]}}{1-p \frac{[M_1]_0}{[M_2]_0}}}{\log \frac{[M_1]_0}{[M_1]} + \log \frac{1-p \frac{[M_1]}{[M_2]}}{1-p \frac{[M_1]_0}{[M_2]_0}}} \quad (2)$$

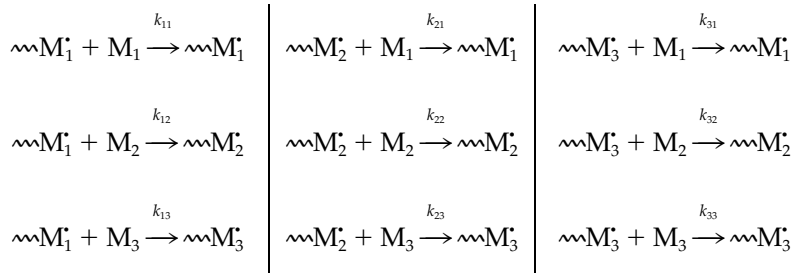
where

$$p = \frac{1-r_1}{1-r_2} \quad (3)$$

and  $[M_1]_0$ ,  $[M_2]_0$  refer to the initial concentration of monomers  $M_1$  and  $M_2$  in the feed;  $[M_1]$  and  $[M_2]$  represent unreacted monomer concentrations.

#### FINEMAN-ROSS METHOD<sup>6</sup>

According to Fineman and Ross, eq. (4) is obtained based on eq. (1):



$$r_2 = \frac{f_1}{1-f_1} \cdot \frac{1-2F_1}{F_1} + \frac{f_1^2}{(1-f_1)^2} \times \frac{1-F_1}{F_1} \cdot r_1 = -G + H \cdot r_1 \quad (4)$$

$f_1$  and  $F_1$  are mol fractions of monomer  $M_1$  in the feed and of unit  $M_1$  in the copolymer formed instantaneously  $F_1$ , respectively.

#### KELEN-TÜDOS METHOD<sup>7,8</sup>

The Kelen-Tüdös method is based on the Fineman-Ross method, with the aim of preventing the nonsymmetrical character of the composition of eq. (4) from affecting the values of  $r_1$  and  $r_2$ , which are determined experimentally.

By setting:

$$\eta = \frac{G}{\alpha + H} \quad \text{and} \quad \xi = \frac{H}{\alpha + H}$$

the instantaneous composition equation can be written as:

$$\eta = \xi \left( r_1 + \frac{r_2}{\alpha} \right) - \frac{r_2}{\alpha} \quad (5)$$

with

$$\alpha = \sqrt{H_{\min} \cdot H_{\max}} \cdot H_{\min} / H_{\max}$$

are minimum and maximum H values.

By plotting  $\eta$  vs.  $\xi$ , a straight line can be obtained, and  $r_1$  and  $-(r_2)/\alpha$  are the values of  $\eta$  for  $\xi = 1$  and for  $\xi = 0$ , respectively.

#### USE OF BINARY REACTIVITY RATIOS TO DESCRIBE TERPOLYMERIZATION SYSTEM<sup>9-11</sup>

In terpolymerization, nine possible propagation reactions can take place as follows:

Several different methods and equations for terpolymer system calculations were described in refs. 10 and 11. The equation of authors Alfrey and Goldfinger has been shown to give good agreement between estimated radical terpolymer compositions and experimental results.<sup>10</sup> Therefore, it was chosen to be applied in this work. Alfrey and Goldfinger<sup>9</sup> derived the following equation to describe terpolymerization:

$$d[M_1]:d[M_2]:d[M_3] = [M_1] \cdot \left[ \frac{[M_1]}{r_{31}r_{21}} + \frac{[M_2]}{r_{21}r_{32}} + \frac{[M_3]}{r_{31}r_{23}} \right] \\ \times \left[ [M_1] + \frac{[M_2]}{r_{12}} + \frac{[M_3]}{r_{13}} \right] : [M_2] \cdot \left[ \frac{[M_1]}{r_{12}r_{31}} + \frac{[M_2]}{r_{12}r_{32}} \right. \\ \left. + \frac{[M_3]}{r_{32}r_{13}} \right] \left[ [M_2] + \frac{[M_1]}{r_{21}} + \frac{[M_3]}{r_{23}} \right] : [M_3] \cdot \left[ \frac{[M_1]}{r_{13}r_{21}} \right. \\ \left. + \frac{[M_2]}{r_{23}r_{12}} + \frac{[M_3]}{r_{13}r_{23}} \right] \left[ [M_3] + \frac{[M_1]}{r_{31}} + \frac{[M_2]}{r_{32}} \right] \quad (6)$$

with  $d[M_1] + d[M_2] + d[M_3] = 1$ , and  $[M_1] + [M_2] + [M_3] = 1$ , where  $[M_i]$  is the molar fraction of monomer  $i$  in feed and  $d[M_i]$  is the instantaneous molar fraction of monomer  $i$  at a certain time.

The  $r$  values shown in this equation are the  $r_1$  and  $r_2$  values of each of the three monomer pairs  $M_1$ - $M_2$ ,  $M_2$ - $M_3$ , and  $M_1$ - $M_3$ . To distinguish these better, each  $r$  value has now two index numbers:

$$\begin{array}{ccc} M_1 - M_2 & M_2 - M_3 & M_1 - M_3 \\ r_1 = k_{11}/k_{12} = r_{12} & r_1 = k_{22}/k_{23} = r_{23} & r_1 = k_{11}/k_{13} = r_{13} \\ r_2 = k_{22}/k_{21} = r_{21} & r_2 = k_{33}/k_{32} = r_{32} & r_2 = k_{33}/k_{31} = r_{31} \end{array}$$

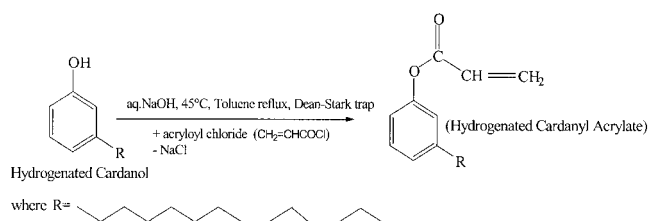
Equation (6) can be used to calculate the instantaneous copolymer compositions.

The chemical composition distribution of the terpolymer is usually plotted in a triangular diagram.

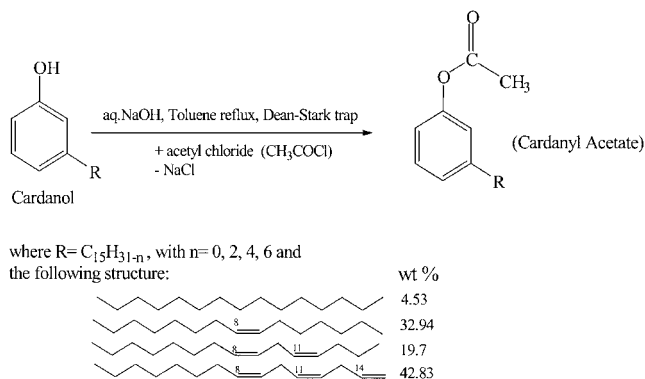
## EXPERIMENTAL

### Materials

Cardanol was recovered from technical cashew nut shell liquid (obtained from Tai Loi company, Viet Nam) by direct vacuum distillation at a reduced pres-



**Scheme 2** Reaction of hydrogenated cardanol and acryloyl chloride to form hydrogenated cardanyl acrylate.



**Scheme 3** Reaction of cardanol and acetyl chloride to form cardanyl acetate.

sure of 5–6 mbar, under nitrogen, and the fraction distilled at 190–210°C was collected.

The hydrogenated cardanol (P440-2), technical chemical grade, used in this study was supplied by Aldrich Company. Acryloyl chloride and acetyl chloride were supplied by Fluka. Styrene (Fluka) was freed from inhibitor by vacuum distillation before using in the copolymerization investigation. Hydroquinone, sodium hydroxide, methyl ethyl ketone peroxide (MEKP, 35 wt % solution in a mixture of diisobutylphthalate and diacetone alcohol), and the solvents were supplied by Merck. Cobalt naphthenate (Co<sup>2+</sup>, 1 wt % solution in toluene) was supplied by Vianova Resins Company (Graz, Austria).

### Preparation of monomers

HCA was synthesized according to reaction Scheme 2, and was carried out as described in ref. [12]. The HCA product was obtained in solid form at room temperatures, with a melting point between 40–45°C and  $d_{20} = 0.9054 \text{ g/cm}^3$ .

CACE was synthesized in the same way according to reaction Scheme 3. CACE obtained is a transparent, yellow liquid with a density  $d_{20} = 0.975 \text{ g/cm}^3$ .

### Instrumentation and experimental procedure

A Perkin-Elmer FTIR spectrometer Model 1600 was used in this work. The FTIR was equipped with a Mettler Instruments FP 52 hotstage.

The liquid samples of S-HCA (or S-CACE and HCA-CACE) were catalyzed using MEKP and cobalt naphthenate (Co<sup>2+</sup>) (4% of the weight of the reactive monomer mixtures). After thorough mixing and minimum delay (less than 2–3 min), one drop of the reactive mixture was placed as a thin film between two NaCl windows, which were then sealed. The window was placed in the hotstage and mounted into the FTIR chamber. The curing reaction for S-HCA, S-CACE, and HCA-CACE was studied isothermally at 120, 130,

TABLE I  
Characteristics of a Copolymerization of Styrene and HCA

Sample	$[S]_0$ (mol/L)	$[HCA]_0$ (mol/L)	$[S]^*$ (mol/L)	$[HCA]^*$ (mol/L)	$f_1$	$F_1$	$\alpha_S$	$\alpha_{HCA}$	Overall conversion $\alpha_T$
S-HCA-1	0.4353	2.4031	0.0570	0.3396	0.1534	0.1437	0.1309	0.1413	0.1397
S-HCA-2	0.8707	2.2763	0.0987	0.3139	0.2767	0.2393	0.1134	0.1379	0.1311
S-HCA-3	2.1624	1.7710	0.1881	0.2033	0.5960	0.4806	0.0720	0.1148	0.0893
S-HCA-4	5.2259	1.0118	0.4462	0.1986	0.8378	0.6920	0.0854	0.1963	0.1034

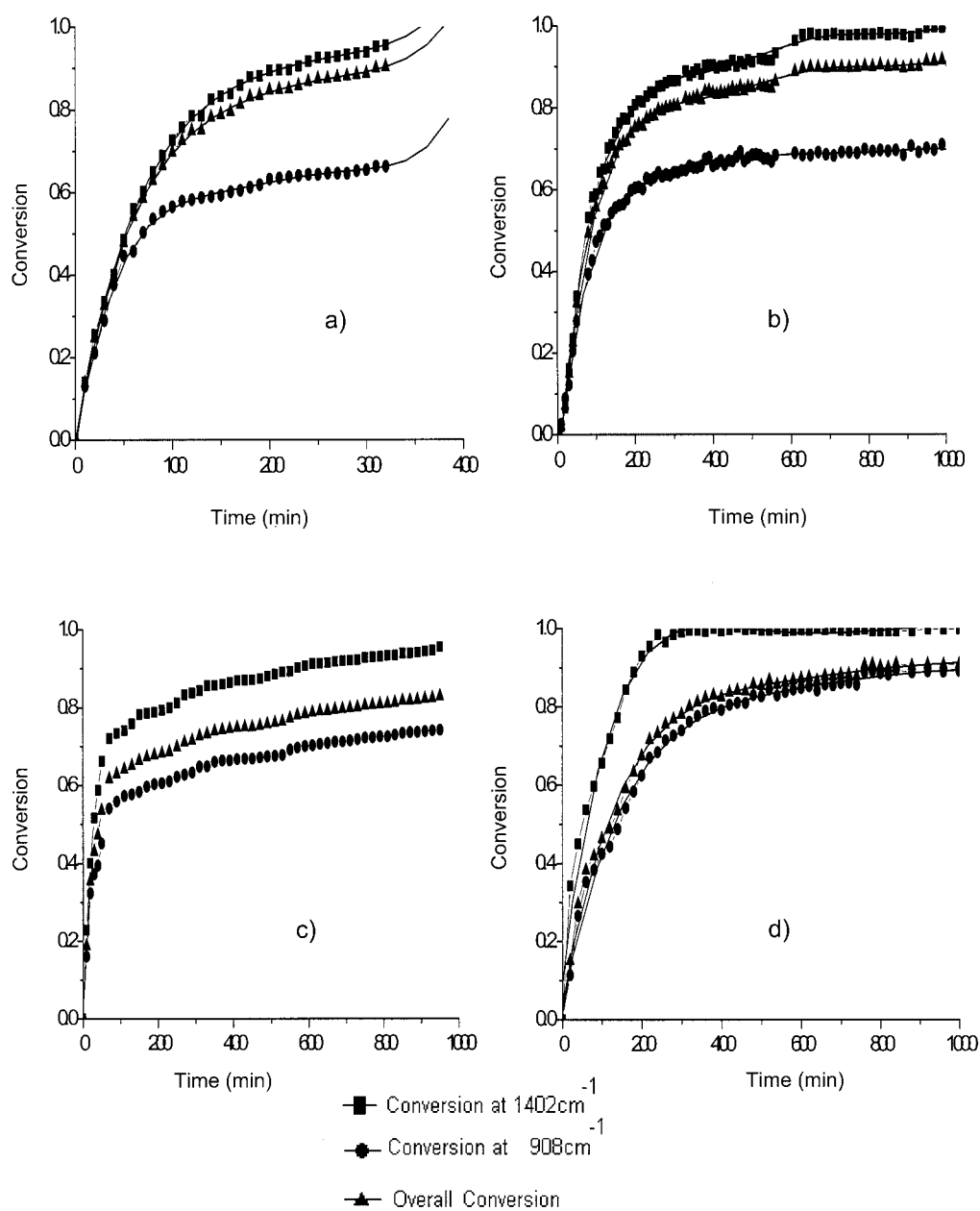
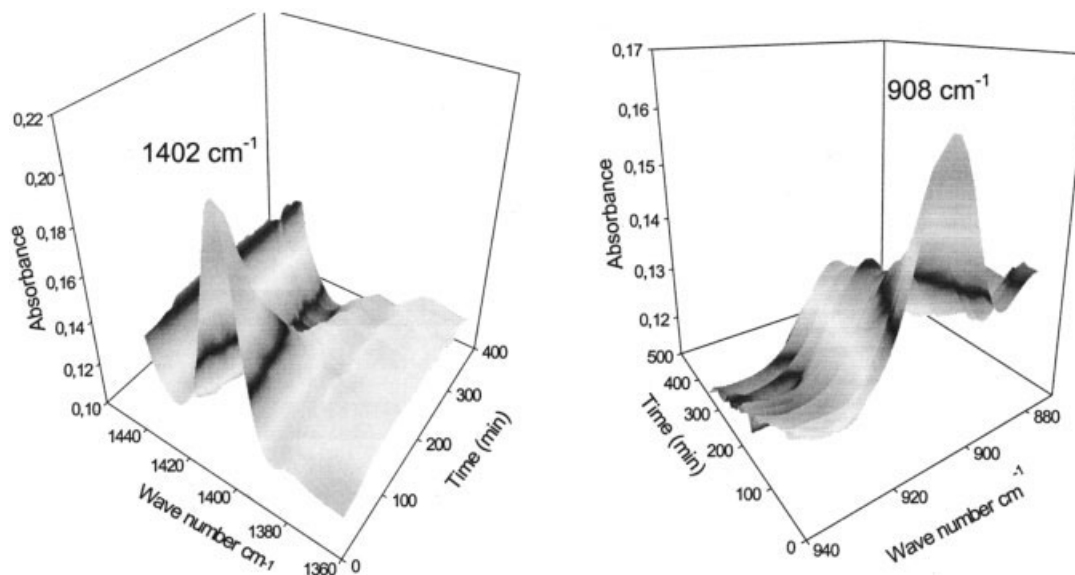


Figure 1 The conversion of S-HCA samples at 120°C by isothermal FTIR measurement. (a) Sample S-HCA-1; (b) sample S-HCA-2; (c) sample S-HCA-3; (d) sample S-HCA-4.



**Figure 2** Selected IR spectra of S-HCA-1 showing the peak changes of functional groups at 1402 and 908  $\text{cm}^{-1}$  at 120°C.

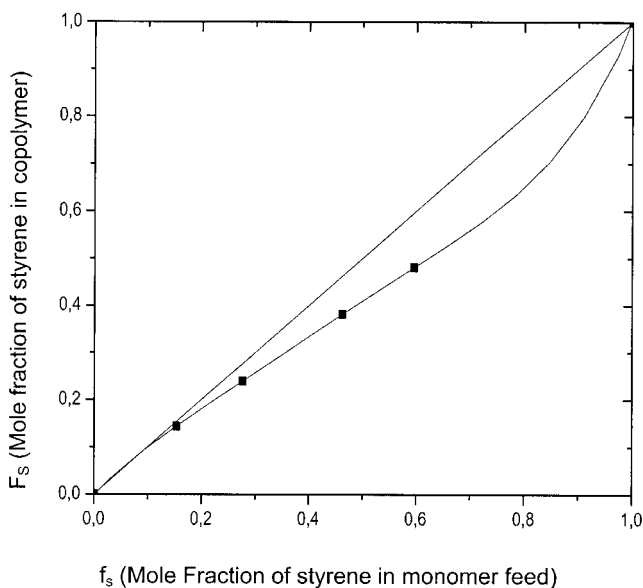
and 150°C by time-resolved FTIR, monitoring the disappearance of peaks for double bonds.

FTIR analysis<sup>13-14</sup>

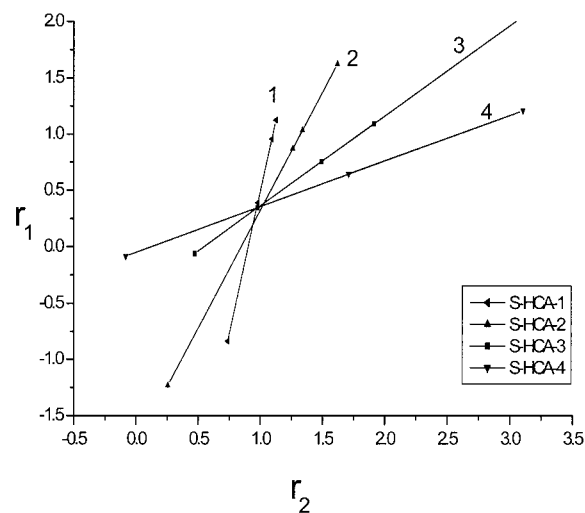
Infrared analysis that can directly measure the concentration of functional groups was used to investigate the copolymerization characteristics of systems S-HCA, S-CACE, HCA-CACE. Furthermore, the reactivity ratios for the radical copolymerization of these monomers with styrene and the ratios for the monomers together were estimated based on a change of the reactive groups in the system by FTIR.

Based on the change of the peak of functional groups at 1402 and 908  $\text{cm}^{-1}$  assigned to the C—H in plane bending vibrations of  $\text{>C=CH}_2$  of HCA (named acrylic double bond) and styrene double bonds, respectively, the concentrations of unreacted double bonds for S-HCA copolymerization were determined. The peak at 982  $\text{cm}^{-1}$ , which is also caused by acrylic double bonds (= acry), was not chosen for the calculation because it overlaps with the styrene peak at 992  $\text{cm}^{-1}$ .

In the case of the S-CACE system, the concentrations of unreacted double bonds were determined at 3008 and 908  $\text{cm}^{-1}$  for the alkyl side chain double bonds of CACE (cardanol double bond) and styrene double bonds.



**Figure 3** Instantaneous compositions of S-HCA copolymers ( $F_s$  vs.  $f_s$  diagram).



**Figure 4** Mayo-Lewis plot for determination of reactivity ratios of the S-HCA system.

In the case of HCA-CACE copolymerization, the concentrations of unreacted double bonds were determined at 1402 and 3008  $\text{cm}^{-1}$  for C—H in plane bending of  $\text{>C=CH}_2$  of HCA and the alkyl side chain double bonds of CACE.

To compensate for a change in sample thickness the FTIR data was normalized to an internal standard peak. In this work, the C—H peak at 2925  $\text{cm}^{-1}$  was chosen as the internal standard for normalizing, and peak height was used instead of area. The determination of the unreacted concentration of monomers in the mixture was calculated according to Beer-Lambert's law.<sup>15-17</sup>

All IR spectra in this study are presented in absorbance units.

The conversion of the reaction can be determined from the change of the normalized absorbances  $A_o$  and  $A_t$  of the monomer functional group before the reaction and after a reaction time  $t$ .

$$\alpha = 1 - A_t/A_o \quad (7)$$

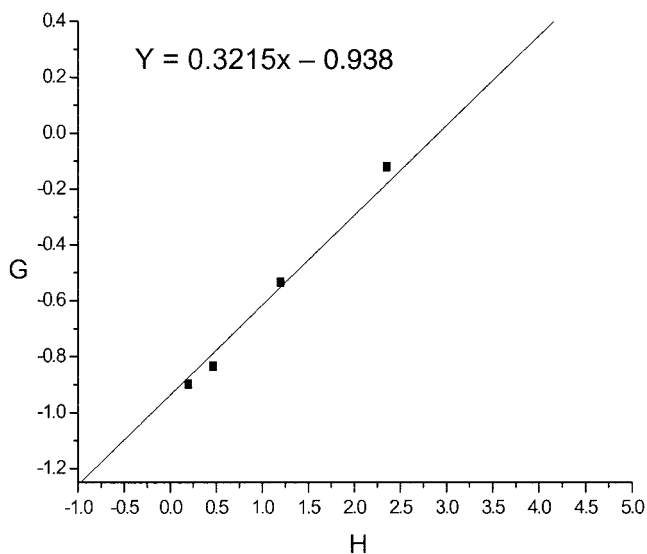
In the case of the S-HCA system, the conversion of mixtures S-HCA is based on the overall consumption of C=C bonds.

The overall conversion of C=C bonds can be expressed as:

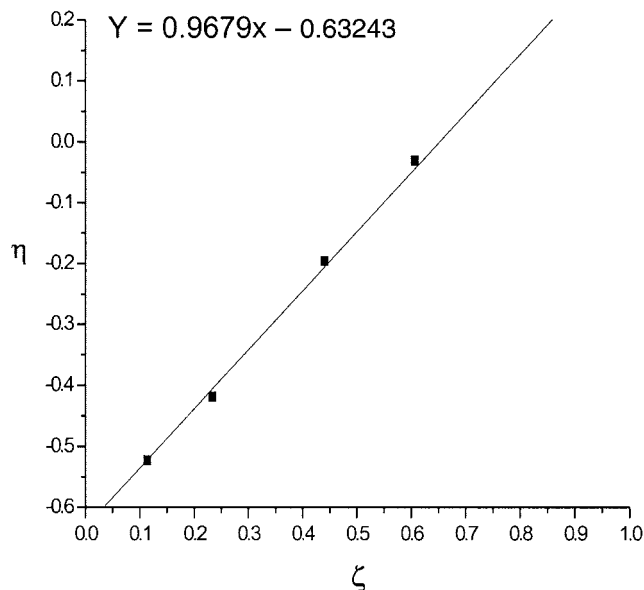
$$\alpha_T = \frac{\alpha_S + I\alpha_H}{1 + I} \quad (8)$$

where

$$I = [\text{HCA}]_o/[\text{S}]_o \quad (9)$$



**Figure 5** Fineman-Ross plot for determination of reactivity ratios of the S-HCA system.



**Figure 6** Kelen-Tüdös plot for determination of reactivity ratios of the S-HCA system.

$\alpha_S$ , the styrene conversion, can be determined from the peak height change at 908  $\text{cm}^{-1}$

$$\alpha_S = 1 - (A_t/A_o)_{908} \quad (10)$$

$\alpha_H$ , the HCA conversion, can be determined from the peak height change at 1402  $\text{cm}^{-1}$

$$\alpha_H = 1 - (A_t/A_o)_{1402} \quad (11)$$

$[\text{S}]_o$ ,  $[\text{HCA}]_o$ ,  $[\text{S}]^*$ , and  $[\text{HCA}]^*$ , which are concentrations of styrene and HCA monomers in the feed and the reacted concentration at the reaction time  $t$ , respectively, are obtained by:

$$[\text{S}]^* = [\text{S}]_o \cdot \alpha_S \quad (12)$$

$$[\text{HCA}]^* = [\text{HCA}]_o \cdot \alpha_H \quad (13)$$

For S-CACE and HCA-CACE systems, all calculations of conversion and concentration of monomers in the reaction system were determined analogously.

**TABLE II**  
Reactivity Ratios of the Copolymerization of S-HCA  
Calculated by Three Different Methods

Method of calculation	$r_1$	$r_2$
Mayo-Lewis	$0.296 \leq r_1 \leq 0.3828$	$0.9142 \leq r_2 \leq 1.0279$
Fineman-Ross	0.322	0.938
Kelen-Tüdös	0.3355	0.964

TABLE III  
Characteristics of Copolymerization of Styrene and CACE

Sample	[S] <sub>0</sub> (mol/L)	[CACE] <sub>0</sub> (mol/L)	[S]* (mol/L)	[CACE]* (mol/L)	<i>f</i> <sub>1</sub>	<i>F</i> <sub>1</sub>	Conversion <i>α</i> <sub>S</sub>	Conversion <i>α</i> <sub>CACE</sub>	Overall conversion <i>α</i> <sub>T</sub>
S-CACE-1	0.9306	2.5468	0.3294	0.3667	0.2676	0.4732	0.3540	0.0708	0.20043
S-CACE-2	1.847	2.2468	0.2261	0.1301	0.4512	0.6348	0.1224	0.0579	0.08699
S-CACE-3	2.7499	1.9512	0.2703	0.0970	0.5849	0.7360	0.0983	0.0497	0.0782
S-CACE-4	4.5156	1.3732	0.8214	0.1372	0.7668	0.8569	0.1819	0.0999	0.16

Because all kinetic measurements have been carried out by FTIR, the instantaneous mol fraction of *F*<sub>1</sub> is calculated by eq. (14):

$$F_1 = \frac{[M_1]_0 \cdot \alpha_{M_1}}{[M_1]_0 \cdot \alpha_{M_1} + [M_2]_0 \alpha_{M_2}} \quad (14)$$

where *α*<sub>M1</sub> and *α*<sub>M2</sub> are obtained from the plots of conversion versus time. These conversions correspond to a chosen overall conversion that is lower than 15%.

## RESULTS AND DISCUSSION

### Reactivity ratios of S-HCA, S-CACE, and HCA-CACE

#### Copolymerization of S-HCA

Data on the copolymerization of styrene and HCA are collected in Table I and the experimental FTIR results are shown in Figure 1, where the conversion is plotted vs. time at the characteristic wave numbers for sample S-HCA-1, S-HCA-2, S-HCA-3, and S-HCA-4, respectively. In Figure 1 the conversion of (= acry) is followed by FTIR at 1402 cm<sup>-1</sup>, the conversion of styrene at 908 cm<sup>-1</sup>, and the overall conversion is calculated by eq. (8).

The peak changes during the reaction of S-HCA are illustrated in Figure 2.

Table I shows characteristics of a copolymerization of Styrene and HCA; [S]<sub>0</sub> and [HCA]<sub>0</sub> are concentrations (mol/L) of styrene and HCA in feed, and [S]\* and [HCA]\* are reacted concentrations at the reaction time *t*. *f*<sub>1</sub> and *F*<sub>1</sub> correspond to mol fractions of styrene monomer in the feed and in the copolymer, respectively. *α*<sub>S</sub> = conversion of styrene, *α*<sub>HCA</sub> = conversion of (= acry).

Figure 3 shows the monomer-copolymer composition curve of the system. The existence of an azeotrope

indicates that both monomer reactivity ratios are less than unity.

By defining styrene as monomer 1, the monomer reactivity ratios *r*<sub>1</sub> and *r*<sub>2</sub> are 0.296 ≤ *r*<sub>1</sub> ≤ 0.3828 and 0.9142 ≤ *r*<sub>2</sub> ≤ 1.0279, respectively, evaluated by the Mayo-Lewis method. The Mayo-Lewis plot is shown in Figure 4.

These values of the reactivity ratios are in agreement with the results obtained by two other methods, Fineman-Ross and Kelen-Tüdös (Figs. 5–6), as can be seen in Table II.

### Copolymerization of S-CACE and HCA-CACE systems

Analogous to the procedure of reactivity ratios calculation for S-HCA, data for the kinetic calculation is obtained by FTIR experiments and the data on the copolymerization of (S and CACE), (HCA and CACE) are presented in Tables III–IV, respectively.

The IR peak changes during the reaction of S-CACE and HCA-CACE are illustrated in Figures 7–8.

Table IV shows characteristics of a copolymerization of HCA and CACE. Symbols are explained in Table I.

Figures 9–10 show the monomer-copolymer composition curve of S-CACE and HCA-CACE systems, respectively.

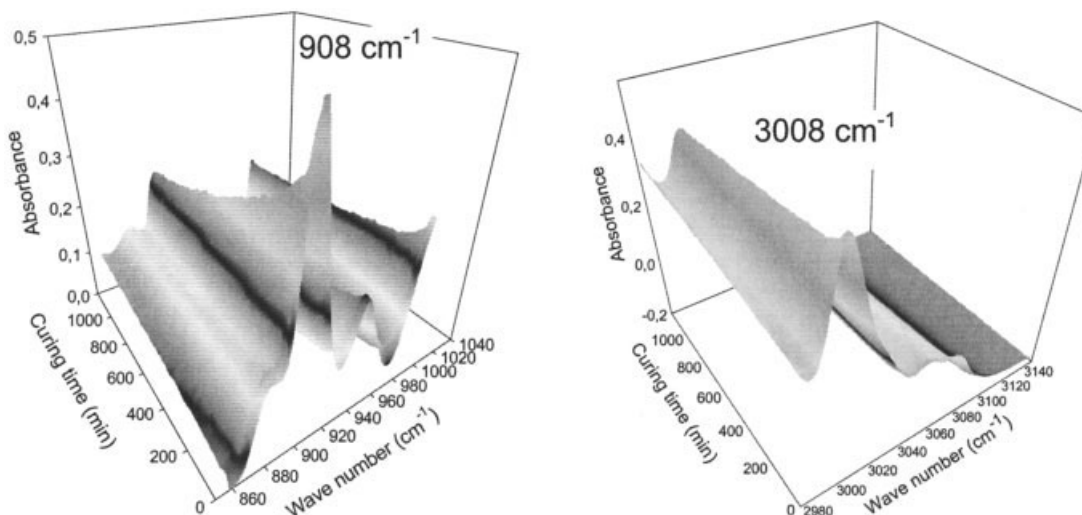
The resulting reactivity ratios for the system S-CACE and HCA-CACE are displayed in Tables V and Table VI. The reactivity ratios determined by the three different methods are in good agreement.

### Structure of copolymers

In the case of S-HCA (cf. Fig. 3) *r*<sub>1</sub> ~ 0.336 (<1); therefore, the styrene-type radical S· in the system of

TABLE IV  
Characteristics of a Copolymerization of HCA and CACE

Sample	[HCA] <sub>0</sub> (mol/L)	[CACE] <sub>0</sub> (mol/L)	[HCA]* (mol/L)	[CACE]* (mol/L)	<i>f</i> <sub>1</sub>	<i>F</i> <sub>1</sub>	HCA- conversion	CACE- conversion	Overall conversion
HCA-CACE-1	0.5365	2.2464	0.0621	0.1930	0.1928	0.2435	0.1158	0.0859	0.0916
HCA-CACE-2	0.7987	1.9510	0.0730	0.1360	0.2905	0.3492	0.0914	0.0697	0.0760
HCA-CACE-3	1.3118	1.3728	0.1333	0.1143	0.4886	0.5384	0.1016	0.0833	0.0922



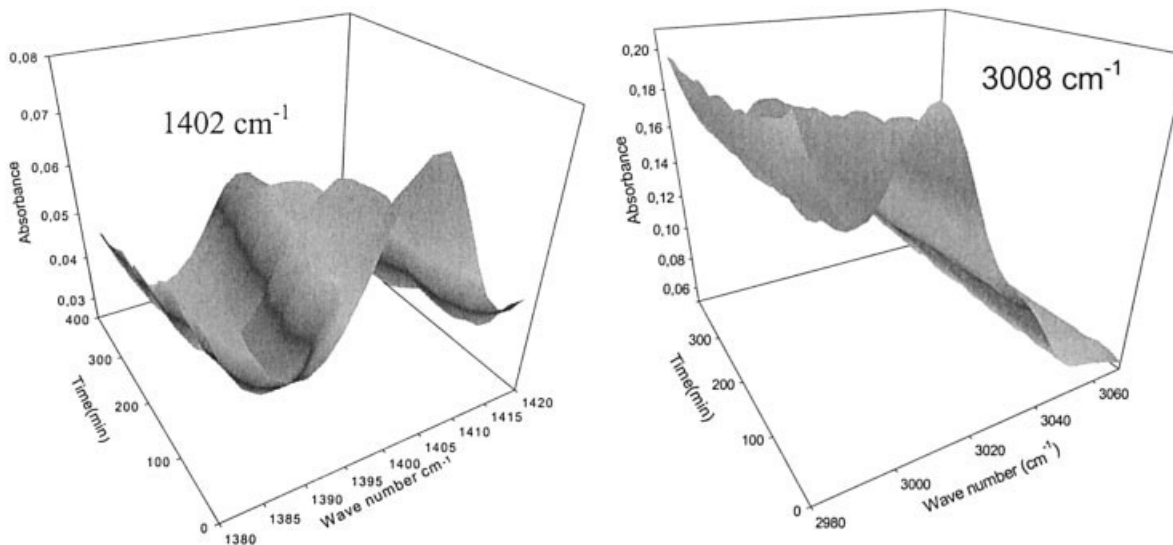
**Figure 7** Selected IR spectra of S-CACE-1 showing the peak changes of functional groups at 908 and 3008  $\text{cm}^{-1}$  at 130°C.

S-HCA has a pronounced preference to react with HCA monomers rather than with styrene monomers, and because  $r_2 \sim 0.964$  (close to 1), there is only a very small preference for copolymerization than for homopolymerization for the free radical  $\text{HCA} \cdot$ . This means both monomers tend to copolymerize. As seen for the S-HCA system in Figure 3, HCA enters the copolymer faster than styrene throughout the whole range of comonomer compositions. The product  $r_1 r_2 = 0.324$  is closer to zero, which indicates that the copolymer formed has a slight tendency to an alternating structure.

In the case of S-CACE (cf. Fig. 9), where the curve is above the diagonal, or with  $r_1 \sim 1.68 > 1$  and  $r_2 \sim 0.295 < 1$ , both free radical types  $\text{S} \cdot$  and  $\text{CACE} \cdot$  easily react

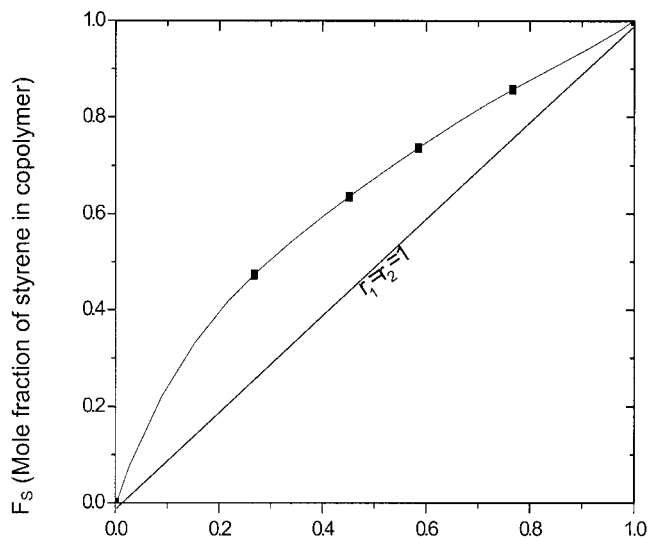
with styrene monomers. The styrene-type radical in the system of S-CACE has a pronounced preference for reacting with styrene monomers rather than with CACE, whereas the CACE-type radical prefers to react with styrene rather than with its own monomer. This means the copolymer formed instantaneously is richer in styrene than the monomer mixture it originates from.

Similar to the case of HCA-CACE (cf. Fig. 10) when  $r_1 > 1$  and  $r_2 < 1$ , both free radical types  $\text{HCA} \cdot$  and  $\text{CACE} \cdot$  easily react with HCA monomer. Because  $r_1$  is close to 1, the copolymer formed instantaneously is slightly richer in HCA than the monomer mixture it originates from. Values  $r_1 \sim 1.057$  and  $r_2 \sim 0.688$  demonstrate that HCA-type radicals will prefer to react with its own monomer, whereas the CACE-type rad-

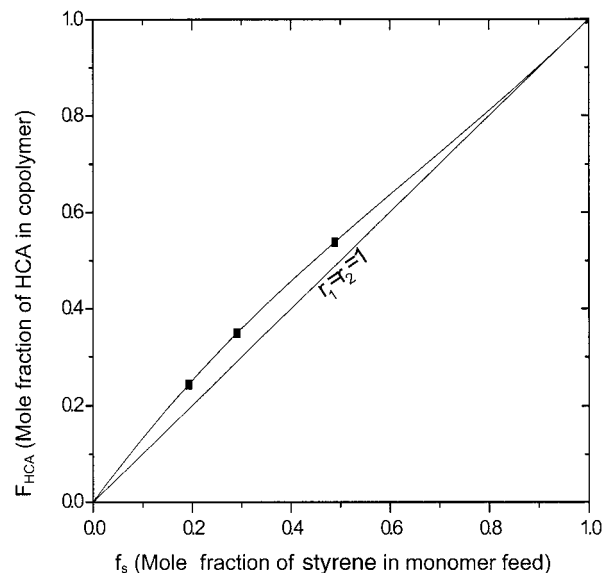


**Figure 8** Selected IR spectra of HCA-CACE-3 showing the peak changes of functional groups at 1402 and 3008  $\text{cm}^{-1}$  at 150°C.





**Figure 9** Instantaneous compositions of S-CACE copolymers ( $F_s$  vs.  $f_s$  diagram).



**Figure 10** Instantaneous compositions of HCA-CACE copolymers ( $F_{HCA}$  vs.  $f_{HCA}$ ).

icals prefer to bind the other monomer, i.e., HCA monomer. In the case of the comonomer pair HCA-CACE,  $r_1$  and  $r_2$  values and its product  $r_1 \cdot r_2 = 0.727$  are close to unity, indicating the reaction system is close to an “ideal copolymerization” or “random copolymer” and shows less tendency for an alternation.

From the three pairs of reactivity ratios of model compounds, a terpolymer model was built for the copolymerization system that consists of S, HCA, and CACE monomers. Using the Copolymer builder module of Cerius<sup>2</sup> Molecular Modeling Package (Molecular Simulations Software GMBH, D-85598 Baldham, Germany) according to their reactivity ratios  $r_{12}$ ,  $r_{21}$ ,  $r_{23}$ ,  $r_{32}$ ,  $r_{13}$  and  $r_{31}$  with a initial monomer compositions of S/HCA were simulated.

Figure 11 shows molecular structures of the S-HCA copolymer with the sequence distribution of monomer units HCA and S along the chain at two different initial monomer compositions of S/HCA = 50/50 and 85/15.

As a result from molecular modeling studies it can be concluded that even at low ratios of cardanol monomer enough flexible side groups are present to enhance mechanical properties of such networks.

**Building the ternary copolymer model for the styrene-HCA-CACE system**

In a polymerization of a three-monomer mixture of styrene-HCA-CACE there are nine possible reactions, as shown above, where S =  $M_1$ , HCA =  $M_2$  and CACE =  $M_3$  with the reactivity ratios as below:

$$\begin{array}{lll}
 M_1 - M_2 (S - HCA) & M_2 - M_3 (HCA - CACE) & M_1 - M_3 (S - CACE) \\
 r_1 = k_{11}/k_{12} = r_{12} = 0.336 & r_1 = k_{22}/k_{23} = r_{23} = 1.057 & r_1 = k_{11}/k_{13} = r_{13} = 1.68 \\
 r_2 = k_{22}/k_{21} = r_{21} = 0.96 & r_2 = k_{33}/k_{32} = r_{32} = 0.688 & r_2 = k_{33}/k_{31} = r_{31} = 0.294
 \end{array}$$

With the two index number reactivity ratios  $r_{12}$ ,  $r_{21}$ ,  $r_{23}$ ,  $r_{32}$ ,  $r_{13}$ , and  $r_{31}$ , the terpolymerization composition of the S-HCA-CACE system is calculated using a computer model and eq. (6) by Alfrey-Goldfinger.

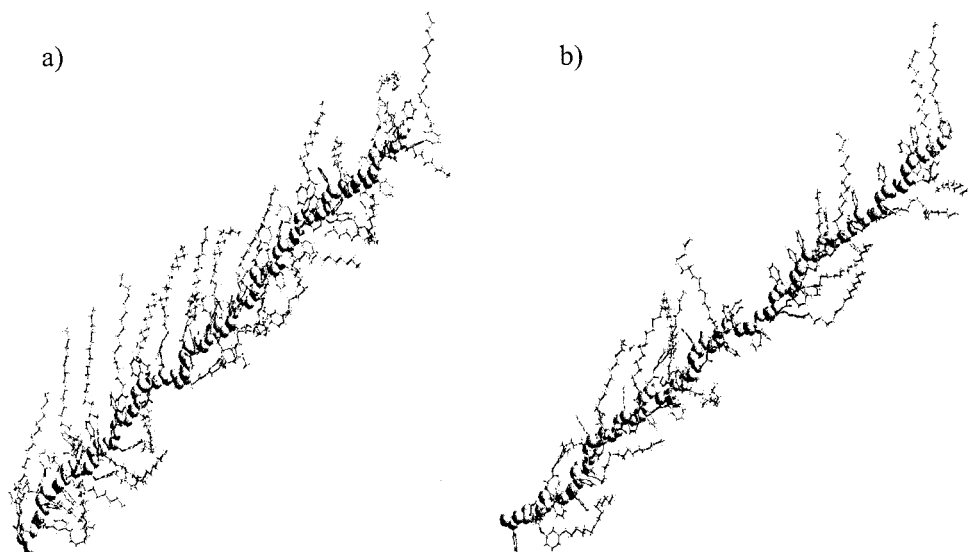
**TABLE V**  
Reactivity Ratios of the Copolymerization of S-CACE Calculated by Three Different Methods

Method of calculation	$r_1$	$r_2$
Mayo-Lewis	$1.4984 \leq r_1 \leq 1.7315$	$0.2063 \leq r_2 \leq 0.3$
Fineman-Ross	1.681	0.2964
Kelen-Tüdös	1.677	0.294

To demonstrate the composition drift occurring in the terpolymerization of S, HCA, and CACE three overall monomer compositions are chosen:  $f_s, f_{HCA}, f_{CACE} = (60, 5, 35), (50, 45, 5),$  and  $(5, 50, 45)$  and are

**TABLE VI**  
Reactivity Ratios of the Copolymerization of HCA-CACE Calculated by Three Different Methods

Method of calculation	$r_1$	$r_2$
Mayo-Lewis	$1.047 \leq r_1 \leq 1.101$	$0.669 \leq r_2 \leq 0.685$
Fineman-Ross	1.052	0.686
Kelen-Tüdös	1.057	0.688

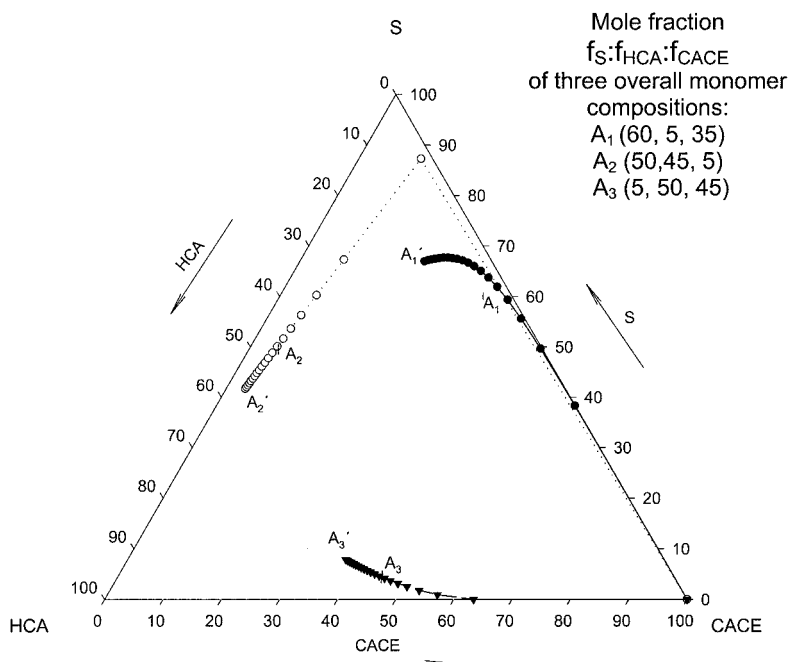


**Figure 11** Molecular model of the S-HCA copolymer with the sequence distribution of monomer units HCA and styrene along the chain: (a) at monomer molar ratios of S/HCA = 50/50; (b) at monomer molar ratios of S/HCA = 85/15.

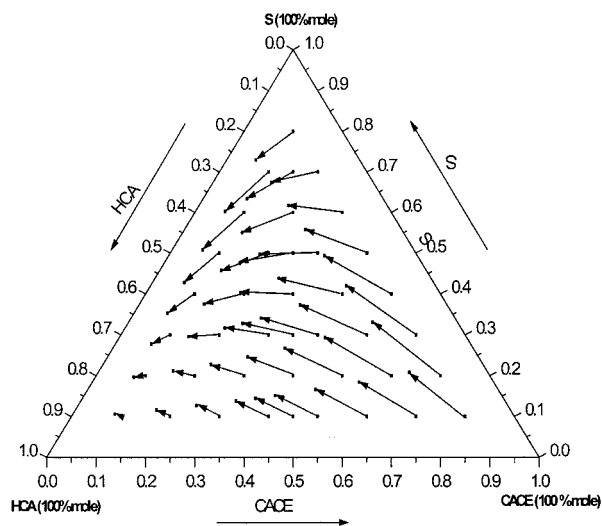
named  $A_1$ ,  $A_2$ ,  $A_3$ . These have increasing fractions of HCA. The results of the ternary copolymerization of  $A_1$ ,  $A_2$ , and  $A_3$  were calculated and represented in a triangular diagram in Figure 12, which shows the course of the composition drift in the radical terpolymerization for S-HCA-CACE system. The lines represent the instantaneous composition of the terpolymers during the polymerization reaction. It can be

seen that they all end at pure CACE. Figure 12 also shows HCA is the most reactive monomer.

Figure 13 shows the initial composition drift in the ternary copolymerization for the system S-HCA-CACE. The arrows represent the overall monomer composition (start of arrow) and the corresponding initial terpolymer composition (end of arrow). It can be seen that there is a strong composition drift.



**Figure 12** The course of the composition drift in radical terpolymerization with varying overall composition:  $A_1$ ,  $A_2$ , and  $A_3$ .  $A_1$ ,  $A_2$ , and  $A_3$  are monomer compositions of S-HCA-CACE reaction system at the start of the polymerization.  $A'_1$ ,  $A'_2$ , and  $A'_3$  are the compositions of the initial terpolymer corresponding to  $A_1$ ,  $A_2$ , and  $A_3$ .



Start of arrow represents the overall monomer composition  
End of arrow represents initial terpolymer composition

**Figure 13** Triangular composition diagrams representing the initial composition drift occurring in S-HCA-CACE radical terpolymerization.

Based on the ternary plots above, it can be concluded that CACE is the least reactive monomer, and HCA the most reactive. This monomer is depleted first, and a copolymer of S and CACE is formed until all S is depleted as well, after which the remaining CACE polymerizes.

### CONCLUSION

FTIR was used effectively to study the copolymerization characteristics between HCA, CACE, with styrene. Based on FTIR results the reactivity ratios of three copolymerization systems S-HCA, S-CACE, and HCA-CACE were determined by three different methods (Mayo-Lewis, Fineman-Ross, and Kelen-Tü-

dos) are  $r_1 \sim 0.336$  and  $r_2 \sim 0.964$ ,  $r_1 \sim 1.68$ , and  $r_2 \sim 0.294$ ,  $r_1 \sim 1.057$ , and  $r_2 \sim 0.688$ , respectively. The results that were determined by three different methods are in very good agreement.

The ability to predict terpolymer compositions with the knowledge of the respective monomer concentrations and reactivity ratios is of significant importance, and helpful to control a composition drift in the radical terpolymerization of the HCA-CACE-S system.

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