## NOVEL COPOLYMERS OF TRISUBSTITUTED ETHYLENES AND STYRENE. I. ALKYL AND ALKOXY RING-SUBSTITUTED ETHYL 2-CYANO-1-OXO-3-PHENYL-2-PROPENYLCARBAMATES

Gregory B. Kharas[a]; Antonia M. Fuerst[a]; Anthony Scola III[a]; Daniel J. Bavirsha[a]; Bradley M. Bernau[a]; Santkileo K. Brown[a]; Pasa Ece[a]; Anna N. Dabrowski[a]; Penny De Angelo[a]; Farrah R. Fatemi[a]; Kenneth Watson[b]

[a] Chemistry Department, DePaul University, Chicago, IL, U.S.A. [b] Rubber Division, Bayer Inc, Sarnia, Canada

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Gregory B. Kharas,[1,*] Antonia M. Fuerst,[1] Anthony Scola III,[1] Daniel J. Bavirsha,[1] Bradley M. Bernau,[1] Santkileo K. Brown,[1] Pasa Ece,[1] Anna N. Dabrowski,[1] Penny De Angelo,[1] Farrah R. Fatemi,[1] and Kenneth Watson[2]

[1]DePaul University, Chemistry Department, 1036 West Belden Avenue, Chicago, IL 60614-3214
[2]Bayer Inc., Rubber Division, Sarnia, Ontario N7T 7M2, Canada

## ABSTRACT

Electrophilic trisubstituted ethylenes, ring-substituted ethyl 2-cyano-1-oxo-3-phenyl-2-propenylcarbamates, $RC_6H_4CH=C(CN)CONHCO_2C_2H_5$ (where R is H, 2-CH$_3$, 3-CH$_3$, 4-CH$_3$, 2-OCH$_3$, 3-OCH$_3$, 4-OCH$_3$,4-OC$_2$H$_5$) were prepared and copolymerized with styrene. The monomers were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and N-cyanoacetylurethane, and characterized by CHN analysis, IR, $^1$H and $^{13}$C NMR. All the ethylenes were copolymerized with styrene ($M_1$) in solution with radical initiation (AIBN) at 70°C. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, $^1$H and $^{13}$C-NMR. The order of relative reactivity ($1/r_1$) for the monomers is 2-CH$_3$ (1.52) > H (1.20) = 3-CH$_3$ (1.20) > 2-OCH$_3$ (1.16) > 3-OCH$_3$ (0.88) > 4-CH$_3$ (0.48) = 4-OC$_2$H$_5$ (0.48) > 4-OCH$_3$ (0.29). Higher T$_g$ of the copolymers in comparison with that of polystyrene indicates

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*Corresponding author. Fax: 773-325-7421; E-mail: gkharas@depaul.edu

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decrease in chain mobility of the copolymer due to the high dipolar character of the TSE structural unit. Gravimetric analysis indicated that the copolymers decompose in the range $200-355°C$.

*Key Words*: Trisubstituted ethylenes; Radical copolymerization; Styrene copolymers

## INTRODUCTION

Previous studies showed that trisubstituted ethylenes (TSE, $CHR^1=CR^2R^3$) containing substituents larger than fluorine exhibit no tendency to undergo polymerization via double bond. This is due to kinetic considerations superimposed on the thermodynamic factor responsible for the difficulty with which 1,1-and 1,2-disubstituted ethylenes polymerize.[1] Radical copolymerization provides the most general method of overcoming problems encountered in homopolymerization of TSE monomers. This approach has been particularly successful in preparing copolymers from electrophilic TSE monomers having double bonds substituted with halo, cyano, and carbonyl groups and electron-rich monosubstituted ethylenes such as styrene, *N*-vinylcarbazole, and vinyl acetate.[2,3]

In continuation of our studies of the monomer structure-reactivity correlation in the radical copolymerization of TS3E monomers,[4−6] we have prepared ring-substituted ethyl 2-cyano-1-oxo-3-phenyl-2-propenylcarbamates, $RC_6H_4CH=C(CN)CONHCO_2C_2H_5$ (where R is H, 2-$CH_3$, 3-$CH_3$, 4-$CH_3$, 2-$OCH_3$, 3-$OCH_3$, 4-$OCH_3$, 4-$OC_2H_5$), and explore the feasibility of their copolymerization with styrene.

## EXPERIMENTAL

### General Procedures

Infrared spectra of the TSE monomers (NaCl plates) and polymers (KBr pellets) were determined with a Nicolet Avatar 360 FT-IR spectrometer. The melting points of the monomers, the glass transition temperatures ($T_g$), and thermal stability of the copolymers were measured by using a TA Instruments model DSC 2010 and TGA 2090. The molecular weight of polymers was determined relative to polystyrene standards in $CHCl_3$ solutions with sample concentrations 0.8% (wt/vol) by gel permeation chromatography using an Alltech 526 HPLC pump at an elution rate of 1.0 mL/min through Styragel HR 0.5, 1, 3, and 4 columns (Waters) at 25°C, a Model 410 refractive index and Viscotek T50A differential viscometer detectors. $^1H$ and $^{13}C$ NMR spectra of 2−4% $CDCl_3$ solutions of monomers and polymers were obtained on a Bruker DRX-500 spectrometer operating at 500.13 MHz for 1H and 125.76 MHz for 13C. Chemical shifts are reported referenced to

TMS as 0 ppm. Proton spectra utilized 64 K data points with a sweep width of 31.4 kHz, a pulse delay of 10 sec and 5000 scans accumulated. Elemental analyses were performed by Quantitative Technologies Inc., New Jersey.

## Synthesis of Monomers

Benzaldehyde, $o$-tolualdehyde, $m$-tolualdehyde, $p$-tolualdehyde, $o$-anisaldehyde, $m$-anisaldehyde, $p$-anisaldehyde, 4-ethoxybenzaldehyde, $N$-cyano-acetylurethane, DMF, and piperidine supplied from Aldrich Chemical Co., were used for monomer synthesis as received. The preparation procedure was essentially the same for all of the TSE monomers. In a typical synthesis, equimolar amounts of $N$-cyanoacetylurethane and an appropriate ring-substituted benzaldehyde were mixed with a small amount of DMF in an Erlenmeyer flask. A few drops of piperidine were added with stirring. The crystalline product of the reaction was isolated by filtration and purified by recrystallization from 2-propanol.

### Ethyl 2-Cyano-1-oxo-3-phenyl-2-propenylcarbamate

Yield 51%; mp 134°C; $^1$H NMR δ 8.2 (s, 1H, CH=), 7.0−8.1 (m, 5H, phenyl), 4.2 (q, 2H, OCH$_2$), 1.4−1.46 (t, 3H, CH$_3$); $^{13}$C NMR δ 158, 155, 150, 134, 132, 129, 116, 103, 64, 14; IR 3268 (m, N-H), 2972 (m, C-H), 2210 (m, CN), 1766 (s, C=O), 1513 (w, C=C), 1190 (s, C-O), 692 (s, C-H out of plane). Anal. Calcd. for C$_{13}$H$_{12}$N$_2$O$_3$: C, 63.71%; H, 5.29%; N, 11.42%; Found: C, 63.32%; H, 5.12%; N, 11.36%.

### Ethyl 2-Cyano-1-oxo-3-(2-Methylphenyl)-2-Propenylcarbamate

Yield 47%; mp 123°C; $^1$H NMR δ 8.4 (s, 1H, CH=), 7.3−8.0 (m, 4H, phenyl), 4.3 (q, 2H, OCH$_2$), 1.3−1.4 (t, 3H, CH$_3$); $^{13}$C NMR δ 158, 156, 150, 134, 131, 129, 116, 103, 63, 14; IR 3262 (m, N-H), 2981 (m, C-H), 2219 (m, CN), 1755 (s, C=O), 1505 (w, C=C), 1196 (s, C-O), 748 (s, C-H out of plane). Anal. Calcd. for C$_{14}$H$_{14}$N$_2$O$_3$: C, 65.11%; H, 5.46%; N, 10.85%; Found: C, 64.98%; H, 5.45%; N, 10.96%.

### Ethyl 2-Cyano-1-oxo-3-(3-Methylphenyl)-2-Propenylcarbamate

Yield 51%; mp 125°C; $^1$H NMR δ 8.3 (s, 1H, CH=), 7.4−7.8 (m, 4H, phenyl), 4.3 (q, 2H, OCH$_2$), 1.3−1.4 (t, 3H, CH$_3$); $^{13}$C NMR δ 158, 156, 150, 139, 135, 132, 131, 129, 128, 116, 103, 63, 21, 14; IR 3270 (m, N-H), 2977 (m, C-H), 2214 (m, CN), 1751 (s, C=O), 1589 (w, C=C), 1109 (s, C-O), 776 (s, C-H out of plane). Anal. Calcd. for C$_{14}$H$_{14}$N$_2$O$_3$: C, 65.11%; H, 5.46%; N, 10.85%; Found: C, 64.95%; H, 5.48%; N, 10.90%.

### Ethyl 2-Cyano-1-oxo-3-(4-Methylphenyl)-2-Propenylcarbamate

Yield 39%; mp 162°C; $^1$H NMR δ 8.5 (s, 1H, CH=), 7.3−8.3 (m, 4H, phenyl), 4.3 (q, 2H, OCH$_2$), 1.4−1.3 (t, 3H, CH$_3$); $^{13}$C NMR δ 162, 158, 155, 150, 145, 131, 130, 128, 116, 101, 63, 36, 31, 22, 14; IR 3270 (m, N-H), 3078 (m, C-H), 2218 (m, CN), 1790 (s, C=O), 1530 (w, C=C), 1183 (s, C-O), 690 (s, C-H out of plane). Anal. Calcd. for C$_{14}$H$_{14}$N$_2$O$_3$: C, 65.11%; H, 5.46%; N, 10.85%; Found: C, 64.96%; H, 5.57%; N, 10.52%.

### Ethyl 2-Cyano-1-oxo-3-(2-Methoxyphenyl)-2-Propenylcarbamate

Yield 56%; mp 122°C; $^1$H NMR δ 8.9 (s, 1H, CH=), 7.0−8.2 (m, 4H, phenyl), 4.3 (q, 2H, OCH$_2$), 1.3−1.4 (t, 3H, CH$_3$); $^{13}$C NMR δ 160, 158, 151, 150, 135, 129, 121, 116, 111, 102, 63, 58, 14; IR 3263 (m, N-H), 2981 (m, C-H), 2208 (m, CN), 1767(s, C=O), 1670 (w, C=C), 1183 (s, C-O), 750 (s, C-H out of plane). Anal. Calcd. for C$_{14}$H$_{14}$N$_2$O$_4$: C, 61.31%; H, 5.14%; N, 10.21%; Found: C, 60.97%; H, 5.18%; N, 10.35%.

### Ethyl 2-Cyano-1-oxo-3-(3-Methoxyphenyl)-2-Propenylcarbamate

Yield 61%; mp 120°C; $^1$H NMR δ 8.3 (s, 1H, CH=), 7.1−8.5 (m, 4H, phenyl), 3.9−4.3 (q, 2H, OCH$_2$), 1.3−1.4 (t, 3H, CH$_3$); $^{13}$C NMR δ 160, 158, 156, 150, 132, 130, 124, 120, 116, 115, 103, 63, 55, 14; IR 3260 (m, N-H), 2973 (m, C-H), 2210 (m, CN), 1780 (s, C=O), 1615 (w, C=C), 1115 (s, C-O), 683 (s, C-H out of plane). Anal. Calcd. for C$_{14}$H$_{14}$N$_2$O$_4$: C, 61.31%; H, 5.14%; N, 10.21%; Found: C, 60.96%; H, 5.18%; N, 10.24%.

### Ethyl 2-Cyano-1-oxo-3-(4-Methoxyphenyl)-2-Propenylcarbamate

Yield 70%; mp 168°C; $^1$H NMR δ 8.3 (s, 1H, CH=), 7.0−8.2 (m, 4H, phenyl), 4.3 (q, 2H, OCH$_2$), 1.3−1.4 (t, 3H, CH$_3$); $^{13}$C NMR δ 164, 158, 155, 150, 134, 124, 117, 115, 99, 63, 56, 14; IR 3321 (m, N-H), 2980 (m, C-H), 2200 (m, CN), 1764 (s, C=O), 1508 (w, C=C), 1164 (s, C-O), 840 (s, C-H out of plane). Anal. Calcd. for C$_{14}$H$_{14}$N$_2$O$_4$: C, 61.31%; H, 5.14%; N, 10.21%; Found: C, 61.17%; H, 5.07%; N, 10.25%.

### Ethyl 2-Cyano-1-oxo-3-(4-Ethoxyphenyl)-2-Propenylcarbamate

Yield 88%; mp 155°C; $^1$H NMR 8.3 (s, 1H, CH=), 7.0−8.0 (m, 4H, phenyl), 4.1−4.3 (q, 2H, OCH$_2$), 1.3−1.5 (t, 3H, CH$_3$), $^{13}$C NMR δ 164, 159, 155, 150, 134, 124, 117, 115, 99, 64, 63, 14; IR 3292 (m, N-H), 3072 (m, C-H), 2209 (m, CN), 1697 (s, C=O), 1584 (w, C=C), 1195 (s, C-O), 850 (s, C-H out of plane). Anal. Calcd. for C$_{15}$H$_{16}$N$_2$O$_4$: C, 62.50%; H, 5.59%; N, 9.72%; Found: C, 62.26%; H, 5.56%; N, 9.83%.
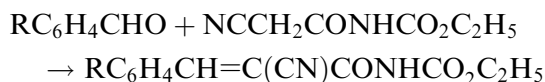
## Copolymerization

Styrene (ST) (Aldrich) was purified by washing with aqueous sodium hydroxide, drying, and subsequently distilling at reduced pressure. Ethyl acetate (Aldrich) was used as received. 2,2′-Azobisisobutyronitrile (AIBN) (Aldrich) was twice recrystallized from ethyl alcohol and then dried under reduced pressure at room temperature. Copolymers of the TSE monomers and styrene were prepared in 25-mL Pyrex screw cap ampoules at equimolar ratio of the monomer feed using 0.0045 mol/L of AIBN at an overall monomer concentration 2 mol/L in 20 mL of ethyl acetate. The copolymerization was conducted at 70°C. After a predetermined time the mixture was cooled to room temperature, and precipitated dropwise in methanol. The crude copolymers were purified by reprecipitation from chloroform solution into an excess of methanol. The composition of the copolymers was determined based on the nitrogen content.

# RESULTS AND DISCUSSION

## Monomer Synthesis

The TSE monomers were synthesized by Knoevenagel condensation[7] of a ring-substituted benzaldehyde with an active hydrogen compound, N-cyanoacetylurethane, catalyzed by a base, piperidine.

$$RC_6H_4CHO + NCCH_2CONHCO_2C_2H_5$$
$$\rightarrow RC_6H_4CH{=}C(CN)CONHCO_2C_2H_5$$

The condensation reaction proceeded smoothly, yielding crystalline products, which were purified by conventional techniques.

## Homopolymerization

An attempted homopolymerization of the TSE monomers in the presence of AIBN did not produce any polymer as indicated by the lack of a precipitate in methanol. The inability of the monomers to polymerize is associated with steric difficulties encountered in homopolymerization of 1,1- and 1,2-disubstituted ethylenes. This type of steric hindrance would increase the activation energy required for addition and slow down the rate of propagation to such an extent as to favor the occurrence of a chain transfer or termination instead. Homopolymerization of ST under conditions identical to those in the copolymerization experiments yielded 18.3% of polystyrene, when polymerized for 30 min.

## Copolymerization

Copolymerization of the ring-substituted ethyl 2-cyano-1-oxo-3-phenyl-2-propenylcarbamates with ST resulted in formation of copolymers (Table 1) with weight-average molecular weights of $1.25 \times 10^4$ to $1.25 \times 10^5$. According to elemental analysis of the copolymers, up to 22% of TSE monomer is present in the copolymers, which is indicative of certain reactivity of the monomers towards ST.

In an attempt to qualitatively correlate the observed monomer reactivities, we considered copolymer composition data obtained at equimolar monomer feed. The relative reactivity of ST in copolymerization with these monomers can be estimated by assuming applicability of the copolymer composition (Eq. (1)) of the terminal copolymerization model:[1]

$$m_1/m_2 = [M_1](r_1[M_1] + [M_2])/[M_2]([M_1] + r_2[M_2]) \tag{1}$$

$m_1$ and $m_2$ are the mole fractions of ST and TSE monomer units in the copolymer, respectively; $[M_1]$ and $[M_2]$ are the concentrations of ST and a TSE in the monomer feed, respectively. In the absence of the self-propagation of TSE monomers ($k_{22} = 0$, $r_2 = 0$), and at equimolar monomer feed ($[M_1]/[M_2] = 1$), Eq. (1) yields:

$$r_1 = m_1/m_2 - 1 \tag{2}$$

or the equation for the relative reactivity of styrene radical $k_{12}/k_{11}$ with TSE monomers:

$$1/r_1 = 1/[(m_1/m_2) - 1] \tag{3}$$

***Table 1.*** Copolymerization of Styrene ($M_1$) and Ring-Substituted Ethyl 2-Cyano-1-oxo-3-phenyl-2-propenylcarbamates, $RC_6H_4CH=C(CN)CONHCO_2C_2H_5$ ($M_2$)

| R ($M_2$) | Yield[a] (wt%) | Nitrogen (wt%) | $m_2$ in Copolymer (mol %) | $M_W \times 10^{-3}$ (daltons) | $T_g$ (°C) | Onset of Decomposition (°C) |
|---|---|---|---|---|---|---|
| H | 15 | 3.91 | 18.8 | 12.5 | 154 | 202 |
| 2-CH$_3$ | 19 | 4.35 | 22.0 | 43.1 | 170 | 319 |
| 3-CH$_3$ | 19 | 3.85 | 18.79 | 125.1 | 177 | 324 |
| 4-CH$_3$ | 15 | 2.19 | 9.65 | 52.6 | 119 | 300 |
| 2-OCH$_3$ | 17 | 3.71 | 18.70 | 53.5 | 147 | 355 |
| 3-OCH$_3$ | 14 | 3.18 | 15.23 | 53.2 | 110 | 323 |
| 4-OCH$_3$ | 16 | 1.5 | 6.40 | 38.9 | 109 | 332 |
| 4-OC$_2$H$_5$ | 10 | 2.15 | 9.69 | 22.2 | 111 | 322 |

[a]Polymerization time was 5 h.

Consideration of monomer reactivities according to Eq. (3) also involves the assumption of minimal copolymer compositional drift at equimolar monomer feed and given conversion. This nonrigorous kinetic treatment nevertheless allows estimation of the reactivity of a styrene-ended polymer radical in reaction with electrophilic monomer.[1] The order of relative reactivity $(1/r_1)$ for the TSE monomers is 2-CH$_3$ (1.52) > H (1.20) = 3-CH$_3$ (1.20) > 2-OCH$_3$ (1.16) > 3-OCH$_3$ (0.88) > 4-CH$_3$ (0.48) = 4-OC$_2$H$_5$ (0.48) > 4-OCH$_3$ (0.29).

## Structure and Thermal Properties

The structure of ST-TSE copolymers was characterized by IR and NMR spectroscopy. IR spectra of the copolymers show overlapping bands in 3300-2600 cm$^{-1}$ region corresponding to C-H stretch vibrations. The bands for the TSE monomer unit are 2235−2245 (w, CN), 1740−1748 (s, C=O), and 1232−1238 cm$^{-1}$ (m, C-O). Benzene rings of both monomers show ring stretching bands at 1492−1499 and 1455−1561 cm$^{-1}$ as well as a doublet 758−767, 690-675 cm$^{-1}$, associated with out of plane C-H bending motions. These bands can be readily identified in styrene copolymers with TSE ethylene monomers containing cyano and carbonyl groups.[4−6] Broadening of the NMR signals in the spectra of the copolymers is apparently associated with head-to-tail and head-to-head structures, which formed though the attack of a styrene-ended radical on both sides of TSE monomer. Thus, Borberly[8] demonstrated that both head-to-tail and head-to-head structures of styrene-ethyl 2-cyano-1-oxo-3-phenyl-2-propenylcarbamates dyads exist in the copolymer. $^1$H NMR spectrum of the ST-TSE copolymers shows a broad double peak in a 5.8−7.8 ppm region corresponding to phenyl ring protons. A broad resonance in a 3.5−4.5 range is assigned to methylene of the ethoxy group and the methine protons of a TSE. The broad resonance in 2.7−3.7 ppm range is assigned to the methine proton of the TSE monomer unit in the head-to-tail ST-TSE dyads. Broad, overlapping resonances in the 1.4−2.7 region are assigned to methine and methylene protons of ST monomer unit in the ST-TSE dyads, which are more subjected to deshielding than the ones in polystyrene. The strong absorption in the 0.7−2.4 ppm range corresponds to ST backbone protons in ST-ST diads. The $^{13}$C NMR spectra also support the suggested skeletal structure of the copolymers. Thus, the assignment of the peaks is as follows: 168 and 165 ppm (C=O), 148−135 p (quaternary carbons of both phenyls), 120−145 ppm (phenyl carbons), 115−118 ppm (CN), 50−60 ppm (methine and quaternary carbons of TSE, and methylene carbon of ST), 45 ppm (ST methine), 40−43 ppm (ST methylene), and 28 ppm (methyl of the ethoxy group). IR and NMR data showed that these are true copolymers, composed of both TSE and ST monomer units.

The copolymers prepared in the present work are all soluble in ethyl acetate, THF, DMF and CHCl$_3$ and insoluble in methanol, ethyl ether, and petroleum ether. They are amorphous and show no crystalline DSC endotherm. Relatively high T$_g$ of the copolymers (Table 1) in comparison with that of polystyrene (T$_g$ = 95°C) indicates decrease of chain mobility of the copolymer due to the high dipolar character of the TSE structural units. Information on the degradation of the copolymers was obtained from thermogravimetric analysis. The decomposition products were not analyzed in this study, and the mechanism has yet to be investigated. Decomposition of all copolymers in air occurs rapidly in one stage in 202−355°C range.

## CONCLUSION

Novel electrophilic trisubstituted ethylenes, ring-substituted ethyl 2-cyano-1-oxo-3-phenyl-2-propenyl carbamates were prepared via a base catalyzed condensation of appropriate substituted benzaldehyde and N-cyanoacetylurethane. The copolymerization of the carbamates with styrene at equimolar monomer feed results in copolymers. The composition of the copolymers was calculated from nitrogen analysis. IR and NMR data showed that these are true copolymers, composed of both TSE and ST monomer units. The order of relative reactivity ($1/r_1$) for the monomers is 2-CH$_3$ (1.52) > H (1.20) = 3-CH$_3$ (1.20) > 2-OCH$_3$ (1.16) > 3-OCH$_3$ (0.88) > 4-CH$_3$ (0.48) = 4-OC$_2$H$_5$ (0.48) > 4-OCH$_3$ (0.29). Higher T$_g$ of the copolymers in comparison with that of polystyrene indicates decrease in chain mobility of the copolymer due to the high dipolar character of the TSE structural unit. The thermal gravimetric analysis indicated that the copolymers decompose in 202−355°C range.

## ACKNOWLEDGMENTS

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