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Novel Copolymers of Trisubstituted Ethylenes with Styrene. I. Alkyl and Alkoxy Phenyl Substituted Methyl 2-Cyano-3-phenyl-2-propenoates

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NOVEL COPOLYMERS OF TRISUBSTITUTED ETHYLENES WITH STYRENE. I. ALKYL AND ALKOXY PHENYL SUBSTITUTED METHYL 2-CYANO-3-PHENYL-2-PROPENOATES

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ABSTRACT

Electrophilic trisubstituted ethylene monomers, phenyl substituted methyl 2-cyano-3-phenyl-2-propenoates, $RC_6H_4CH=C(CN)CO_2CH_3$ (where R is o-CH_3O-, m-CH_3O-, p-CH_3O, and p-C_2H_5-), were prepared and characterized. Novel copolymers of the propenoates and styrene were prepared at equimolar monomer feed composition by solution copolymerization in the presence of a radical initiator at 80°C. The composition of the copolymers was calculated from nitrogen analysis and the structure was analyzed by IR, proton and carbon-13 NMR. High glass

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transition temperatures of the copolymers in comparison
with that of polystyrene indicates a substantial
decrease in chain mobility of the copolymer due to the
high dipolar character of the trisubstituted monomer
unit.

INTRODUCTION

Early studies of substituted ethylenes showed that the
reactivity of the monomers in radical polymerization
depends on their polarity, resonance stabilization and
steric effects (1). Although steric difficulties
preclude homopolymerization of most tri- and
tetrasubstituted olefins, their copolymerization with a
monosubstituted alkene makes it possible to overcome
these steric problems. Copolymerization of electron-
deficient trisubstituted alkenes carrying cyano, halo,
and/or carboalkoxy substituents with such electron-rich
monomers as styrene (2,3), vinyl acetate (4), N-vinyl
carbazole (3), and N-vinylpyrrolidone (5) show a
tendency towards the formation of alternating
copolymers. Copolymerization of the electrophilic
trisubstituted ethylenes and vinyl ethers, which do not
undergo radical homopolymerization led to equimolar
alternating copolymers (6). The enhancement of
reactivity of substituted ethylenes has been explained
by considering the interaction between an electron-
donor radical and an electron-acceptor monomer (or vice
versa) (7) or homopolymerization of monomer donor-
acceptor complexes (8).
In our studies of the monomer structure-monomer
reactivity correlations in radical copolymerization of
trisubstituted ethylenes, it was of interest to prepare
phenyl substituted methyl 2-cyano-3-phenyl-2-

propenoates, $RC_6H_4CH=C(CN)COOCH_3$ (where R is o-CH_3O-, m-CH_3O-, p-CH_3O-, and p-C_2H_5-), and explore the feasibility of their copolymerization with an electron-rich olefin like styrene.

EXPERIMENTAL

General Procedures: Infrared spectra were determined with a Perkin Elmer 1710 FT-IR spectrometer. Samples in CH_2Cl_2 solution were cast on a NaCl plates followed by evaporation in a vacuum oven. Melting points of the monomers (measured as the beginning and the end of the melting endotherm) and glass transition temperatures (T_g) of the copolymers were measured by using a DSC module of STA 625 thermal analyzer (Polymer Laboratories, Inc.). The molecular weight of polymers was determined relative to polystyrene standards in chloroform solutions with sample concentrations 0.8% (wt/vol) by gel permeation chromatography (GPC) using a Waters Model 510 pump at an elution rate of 1.0 mL/min, a Model 410 refractive index detector, a linear ultrastyragel column and Millenium software. ^{1}H and ^{13}C NMR spectra of 4-10% $CDCl_3$ solutions of monomers and polymers were obtained on a Bruker Omega 400WB spectrometer with 9.4T 89 mm bore magnet at room temperature. Parameters for the proton spectra were 3 us pulse width ($\approx$30°), pulse delay 2s, 16384 acquisition points, 32 scans; for the carbon spectra: 6.5 us pulse width ($\approx$30°), pulse delay 3s, 16384 acquisition points, 128 scans, with broadband proton decoupling. Elemental analyses were performed by Quantitative Technologies Incorporated (New Jersey). **Synthesis of Monomers:** 4-Ethylbenzaldehyde (98%), 3-anisaldehyde (97%), methyl cyanoacetate (99%), and

piperidine (99%) supplied from Aldrich Chemical Co., and 4-anisaldehyde (97%) and 2-anisaldehyde (97%) supplied from Pfaltz and Bauer were used for monomer synthesis as received, without additional purification. The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of methyl cyanoacetate and an appropriate aldehyde were mixed with a small amount of N,N-dimethylformamide in an Erlenmeyer flask. A few drops of piperidine were added with stirring. The product of the reaction was isolated by filtration and purified by crystallization from 2-propanol.

Methyl (E)-2-cyano-3-(4-ethylphenyl)-2-propenoate.
Yield 62%; mp 61-64°C; ^{1}H NMR δ 8.3 (s, 1H, CH=), 7.9, 7.3 (d, 4H, phenyl), 3.9 (s, 3H, OCH$_3$), 2.7 (q, 2H, CH$_2$), 1.3 (t, 3H, CH$_3$); ^{13}C NMR δ 163.0 (C=O), 155.0 (CH=), 150.7 (Et-C), 131.2, 128.8, 128.7 (Ph), 115.6 (C≡N), 100.9 (C=), 53.1 (CH$_3$O), 28.9 (CH$_2$), 14.8 (CH$_3$); IR (NaCl) 3000 (m, C-H), 2226 (s, C≡N), 1736 (s, C=O), 1602, 1460 (s, CH$_2$ in plane), 1209 (s, C-O-CH$_3$), 763, 705 (s, CH out of plane); Anal. Calcd for C$_{13}$H$_{13}$NO$_2$: C, 72.55; H, 6.04; N, 6.54. Found: C, 72.51; H, 6.04; N, 6.54.

Methyl (E)-2-cyano-3-(4-methoxyphenyl)-2-propenoate.
Yield 60%; m.p. 102-104°C (lit.(9) 104-106°C); ^{1}H NMR δ 8.3 (s, 1H CH=), 8.1, 7.1 (d, 4H phenyl), 3.9 (s, 3H, CO$_2$CH$_3$), 3.8 (s, 3H, PhOCH$_3$); ^{13}C NMR δ 164.8 (C=O), 163.8 (O-C, Ph), 154.9 (CH=), 134.3, 125.1, 115.6 (Ph), 116.6 (C≡N), 99.7 (C=), 56.1 (CH$_3$O-Ph), 53.3 (CH$_3$OCO); IR (NaCl) 3050 (m, C-H), 2800 (m, C-H), 2223 (s, C≡N), 1731 (s, C=O), 1592 (m), 1513 (m, C=C), 1266 (s, C-O-CH$_3$), 740 (s, CH out of plane). Anal. Calcd for

$C_{12}H_{11}NO_3$: C, 66.34; H, 5.07; N, 6.48. Found: C, 66.19; H, 5.05; N, 6.48.

Methyl (E)-2-cyano-3-(3-methoxyphenyl)-2-propenoate. Yield 71%; m.p. 67-72°C, ^{1}H NMR δ 8.3 (s, 1H, CH=), 7.6-7.1 (m, 4H phenyl), 3.9 (s, 3H, CO_2CH_3), 3.8 (s, 3H, $PhOCH_3$), ^{13}C NMR δ 162.7 (C=O), 159.7 (O-C, Ph), 155.0 (CH=), 132.4, 130.0, 124.1, 120.0, 114.3 (Ph), 115.3 (C≡N), 102.4 (C=), 55.2 (CH_3O-Ph), 53.2 (CH_3OCO); IR (NaCl) 2955 (m, C-H), 2225 (m, C≡N), 1737 (s, C=O), 1608 (s, C=C), 1247 (s, C-O-CH_3), 740 (s, CH out of plane). Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.34 H, 5.07, N, 6.48. Found: C, 66.19, H, 5.07 N, 6.52.

Methyl (E)-2-cyano-3-(2-methoxyphenyl)-2-propenoate. Yield: 53.3%; m.p. 105-109°C (lit.(9) 111-112°C); ^{1}H NMR δ 8.7 (s, 1H, CH=), 8.3-6.9 (m, 4H, phenyl), 3.9 (s, 6H, 2(OCH_3); ^{13}C NMR δ 163.0 (C=O), 159.0 (O-C, Ph), 149.6 (CH=), 134.9, 129.0, 120.6, 120.2, 111.0 (Ph), 115.6 (C≡N), 101.5 (C=), 55.5 (CH_3OPh), 53.0 (CH_3OCO); IR (NaCl) 2950 (m, C-H), 2225 (s, C≡N), 1737 (s, C=O), 1600 (s, C=C), 1270, 1249 (s, C-O-C), 760 (s, CH out of plane). Anal. Calcd for $C_{12}H_{11}NO_3$: C, 66.34; H, 5.07; N, 6.48. Found: C, 66.22; H, 5.04; N, 6.57.

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'-Azobisisobutironitrile (AIBN) (Aldrich) was twice recrystallized from ethyl alcohol and then dried under reduced pressure at r.t. Copolymers of the trisubstituted ethylenes and styrene were prepared in 50-Ml Pyrex screw cap ampules at an equimolar ratio of the monomer feed using 0.0045 mole/L of AIBN at an overall monomer concentration 2 mole/L in 20 ml of

ethyl acetate. The copolymerization was conducted at
80°C. After a predetermined time the mixture was cooled
to r.t. and precipitated by dropwise addition to
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 trisubstituted ethylene monomers were prepared
according to the general procedure of Knoevenagel
condensation (10) by reacting an appropriate ring-
substituted benzaldehyde with methyl cyanoacetate, as
described in the experimental section.

$$RC_6H_4CHO + NCCH_2CO_2CH_3 ---> RC_6H_4CH=C(CN)CO_2CH_3$$
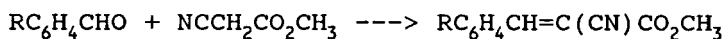
The condensation reaction proceeded smoothly, yielding
crystalline products, which were purified by
conventional techniques. The ^{13}C NMR analysis of the
monomers showed the presence of a single (E)-isomer
with the ester group trans to the ß-substituent, which
is consistent with the NMR data on a variety of alkyl
2-cyano-3-phenyl-2-propenoates (11,12).

Homopolymerization

An attempted homopolymerization of the trisubstituted
ethylenes in the presence of AIBN did not produce any
polymer on the precipitation in methanol. Inability of
the monomers to polymerize is associated with steric
difficulties encountered in homopolymerization of 1,1-
and 1,2-disubstituted ethylenes (1). This type of
steric hindrance would increase the activation energy
required for addition and slow down the rate of

propagation to such extent as to favor the occurrence
of chain transfer or termination step instead.
Homopolymerization of styrene under conditions
identical to those in copolymerization experiments
yielded 18.3% of polystyrene, when polymerized for 30
min.

Copolymerization

Novel trisubstituted ethylene monomers were
copolymerized with styrene at equimolar feed ratios in
ethyl acetate at 80°C in the presence of AIBN. The
choice of the solvent was based on solubility of the
electrophilic monomer at 1 mol/L concentration. AIBN
was chosen due to its low susceptibility to transfer
(13). Copolymerization of phenyl substituted methyl
2-cyano-3-phenyl-2-propenoates with styrene resulted in
formation of copolymers (Table 1).
According to elemental analysis of the copolymers, a
substantial amount of trisubstituted ethylene monomer
is present in the copolymers, which is indicative of
relatively high reactivity of the monomers towards
styrene.
In an attempt to qualitatively correlate the observed
monomer reactivities, we considered copolymer
composition data obtained at equimolar monomer feed.
The relative reactivity of styrene in copolymerization
with these monomers can be estimated by assuming
applicability of the copolymer composition equation (I)
of the terminal copolymerization model (1),
$$m_1/m_2 = [M_1](r_1[M_1] + [M_2])/[M_2]([M_1] + r_2[M_2]) \quad (I).$$
m_1 and m_2 are mole fractions of styrene and
trisubstituted ethylene monomer units in the copolymer,
respectively; $[M_1]$ and $[M_2]$ are the concentrations of

TABLE 1.

Copolymerization of styrene (M_1) and phenyl substituted

methyl 2-cyano-3-phenyl-2-propenoates (M_2),

$R-C_6H_4CH=C(CN)CO_2CH_3$

R	Time,	Yield,	M_2 in copolymer	M_w	T_g
	hr	wt%	mol%	x 10^{-3}	°C
p-C_2H_5	1.0	11.5	36.0	39.6	195
p-OCH_3	4.0	12.9	27.0	74.0	210
m-OCH_3	0.5	7.53	41.4	66.7	220
o-OCH_3	0.5	3.07	29.2	39.0	172

styrene and trisubstituted ethylene in the monomer
feed, respectively. In the absence of trisubstituted
ethylene self-propagation ($k_{22} = 0$, $r_2 = 0$) and at
equimolar monomer feed ($[M_1]/[M_2] = 1$), eq I yields

$$r_1 = m_1/m_2 - 1 \qquad (II)$$

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

$$1/r_1 = 1/(m_1/m_2) - 1 \qquad (III)$$

Consideration of monomer reactivities according to
eq III involves also 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. The order of
reactivity ($1/r_1$) for the four trisubstituted ethylene

monomers is m-CH$_3$O- (2.83) > p-C$_2$H$_5$- (1.29) > o-CH$_3$O-
(0.70) > p-CH$_3$O- (0.59); for methyl 2-cyano-3-phenyl-2-
propenoate (unsubstituted ring) $1/r_1$ is 1.3 (15). The
significant conclusion from the early copolymerization
studies (1) is that the $1/r_1$ and the tendency toward
alternation of monomer units in the copolymer increases
as the difference in polarity between two monomers
increases. Based on information on the effect of
substituents on electrophilic aromatic substitution,
alkoxy and alkyl groups are moderately and weakly
activating $ortho$-$para$ directors (14). The introduction
of electron-releasing alkyl and alkoxy groups into the
aromatic ring would be expected to increase electron
density of the double bond, especially, if the
substituent is in the $ortho$ or $para$ position, thus
decreasing (lowering electrophilicity) the reactivity
of the trisubstituted ethylene monomer. The most
reactive electrophilic trisubstituted monomer should be
the one with an electron-donating group (OCH$_3$) in $meta$
position. Since the values of relative reactivities
were single-point determinations, the reactivities may
not be exact, but the trend definitely indicates that
the $meta$-isomers are most reactive. The influence of
the substitution on the resonance stability of the free
radical is not obvious, since apparently the attack of
a styrene-ended polymer radical on both sides of the
trisubstituted ethylene monomer is possible. Thus,
Borberly (15) has demonstrated that both head-to-tail
and head-to-head structures of styrene-methyl 2-cyano-
3-phenyl-2-propenoate dyads exist in the copolymer.
More detailed information on the copolymer composition
at different monomer feed ratios would be necessary for
the application of copolymerization models that would
allow prediction of copolymer composition.

Physical Properties

The copolymers prepared in the present work are all amorphous powders, soluble in DMF, $CHCl_3$ and insoluble in methanol and in heptane, and petroleum ether. IR and NMR data showed that these are true copolymers, composed of both trisubstituted ethylene and styrene monomer unit. High T_g of the copolymers (Table 1) in comparison with that of polystyrene ($T_g=95°C$) indicates substantial decrease of chain mobility of the copolymer due to high dipolar character of the propenoate structural unit.

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