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Novel copolymers of trisubstituted ethylenes with styrene – 7. Methyl 2-cyano-3-dihalophenyl-2-propenoates

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Summary

Methyl 2-cyano-3-dihalophenyl-2-propenoates, $R_2C_6H_3CH{=}C(CN)CO_2CH_3$ (R_2=2,4-difluoro, 2,5-difluoro, 2,6-difluoro, 3,4-difluoro, 3,5-difluoro, and 2-chloro-6-fluoro), were prepared by the piperidine catalyzed Knoevenagel condensation of corresponding disubstituted benzaldehydes and methyl cyanoacetate. Novel copolymers of the propenoates and styrene were prepared at equimolar monomer feed by solution copolymerization in the presence of a radical initiator. The order of relative reactivity ($1/r_1$) was 2,5-difluoro (2.11) > 2,6-difluoro (1.84) > 3,5-difluoro (1.71) > 2,4-difluoro (1.4) > 3,4-difluoro (0.65) > 2-chloro-6-fluoro (0.59). The copolymers were characterized by IR, ^1H and ^{13}C NMR, GPC, DSC and TGA. High glass transition temperatures of the copolymers compared that of polystyrene indicates a substantial decrease in chain mobility of the copolymers due to the high dipolar character of the trisubstituted ethylene monomer unit.

Introduction

Trisubstituted ethylenes (TSE) containing substituents larger than fluorine exhibit no tendency to undergo radical polymerization, 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. Hall *et al.*, in pioneering studies on copolymerization of electron-poor TSE monomers, showed that these monomers copolymerize readily with monosubstituted electron-rich monomers like styrene, vinyl acetate, vinyl ethers, and *N*-vinylcarbazole [2].

In continuation of our studies of the monomer structure-reactivity correlation in radical copolymerization of TSE monomers [3-5], we have prepared methyl 2-cyano-

3-dihalophenyl-2-propenoates, $R_2C_6H_3CH{=}C(CN)CO_2CH_3$ where R_2 is 2,4-difluoro (24DF), 2,5-difluoro (25DF), 2,6-difluoro (26DF), 3,4-difluoro (34DF), 3,5-difluoro (35DF), and 2-chloro-6-fluoro (2C6F), and explored the feasibility of their copolymerization with styrene (ST).

Experimental

General procedures

Infrared spectra of the TSE monomers were obtained with a 1710 Perkin Elmer FT-IR spectrometer. Melting points of monomers and glass transition temperatures of the copolymers were measured using a DSC-TGA module of an STA 625 thermal analyzer (Polymer Laboratories, Inc.). ^1H and ^{13}C NMR were obtained on a Bruker WP270SY spectrometer operating at 200.13 MHz for ^1H and 50.33 MHz for ^{13}C. All NMR spectra were obtained on 10% solutions in $CDC1_3$ at ambient temperature. The molecular weights of polymers were determined relative to polystyrene standards in chloroform solution with sample concentrations 0.8% (wt/vol) by gel permeation chromatography using a Waters Model 510 pump at an elution rate of 1.0 mL/min through 500, 1000 and 10,000 Å Phenogel (Phenomenex) columns at 35°C, a Model 410 refractive index detector, and Millennium software. Atomic charge distributions were calculated (AM1) by using HYPERCHEM software (AUTODESK, Inc.). Elemental analyses were performed by Quantitative Technologies Inc. (New Jersey).

Synthesis of monomers:

2,4-Difluorobenzaldehyde, 2,5-difluorobenzaldehyde, 2,6-difluorobenzaldehyde, 3,4-difluorobenzaldehyde, 3,5-difluorobenzaldehyde, and 2-chloro-6-fluorobenzaldehyde, methyl cyanoacetate, and piperidine, supplied from Aldrich Chemical Co., were used for monomer synthesis as received. The preparation procedure was essentially the same for all the monomers. In a typical synthesis, equimolar amounts of methyl cyanoacetate and an appropriately substituted benzaldehyde were mixed with N,N-dimethylformamide in an Erlenmeyer flask. A few drops of piperidine were added at the start of the reaction with stirring at room temperature. The product was isolated by filtration and purified by repeated recrystallizations from 2-propanol.

Methyl (*E*)-2-cyano-3-(2,4-difluorophenyl)-2-propenoate. Yield 33.7 %; m.p. 107°C; ^1H NMR δ 4.0 (s, 3H, $-OCH_3$), 6.9-7.3 (m, 3H, Ph-H), 8.4-8.5 (s, CH=); ^{13}C NMR δ 163 (C=O), 162, 159, 146, 130, 116 (Ph), 114 (CN), 105 (C=), 53 (CH_3); IR (NaCl) 2956.0 (m, C-H), 2227 (m, CN), 1738 (s, C=C), 1612 (s, C=C), 1248 (s, C=O), 757 (s, C-H out of plane). Anal. Calcd for $C_{11}H_7F_2NO_2$: C, 59.19; H, 3.14; N, 6.28. Found: C, 58.95; H, 3.07; N, 6.23.

Methyl (*E*)-2-cyano-3-(2,5-difluorophenyl)-2-propenoate. Yield 80.1%; m.p. 103°C; ^1H NMR δ 3.9 (s, 3H, $-OCH_3$), 7.1-8.0 (m, 3H, Ph-H), 8.4 (s, 1H, CH=); ^{13}C NMR δ 162 (C=O), 161, 155, 145, 122, 117, 114 (CN), 106 (C=), 53 (CH_3); IR (NaCl) 2956.0 (m, C-H), 2227 (m, CN), 1738 (s, C=C), 1612 (s, C=C), 1248 (s, C=O), 757 (s, C-H out of plane). Anal. Calcd for $C_{11}H_7F_2NO_2$: C, 59.19; H, 3.14; N, 6.28. Found: C, 59.70; H, 3.12; N, 6.35.

Methyl (*E*)-2-cyano-3-(2,6-difluorophenyl)-2-propenoate. Yield 66.6%; m.p. 104°C; ^1H NMR δ 4.0 (s, 3H, $-OCH_3$), 6.9-7.6 (m, 3H, Ph-H), 8.3 (s, 1H, CH=); ^{13}C

NMR δ 163 (C=O), 162, 157, 143, 134, 110 (Ph), 114 (CN), 54 (-CH_3); IR (NaCl) 2954 (m, C-H), 2247 (m, C≡N), 1748 (s, C=O), 1624 (s, C=C), 1252 (s, C-O-CH_3), 763 (s, C-H out of plane). Anal. Calcd for $C_{11}H_7F_2NO_2$: C, 59.19; H, 3.14; N, 6.28. Found: C, 59.78; H, 3.26; N, 6.30.

Methyl (*E*)-2-cyano-3-(3,4-difluorophenyl)-2-propenoate. Yield 45.9%; m.p. 113°C; ^{1}H NMR δ 3.9 (s, 3H, -OCH_3), 6.9-7.6 (m, 3H, Ph-H), 8.3 (s, 1H, CH=); ^{13}C NMR δ 162 (C=O), 161, 157, 147, 135, 126, 120, 112 (Ph), 114 (CN), 54 (CH_3); IR (NaCl) 2922, 2853 (m, C-H), 2220 (m, C≡N), 1712 (s, C=O), 1580, 1456 (s, C=C), 1303, 1265 (s, C-O-CH_3), 761 (s, C-H out of plane). Anal. Calcd for $C_{11}H_7F_2NO_2$: C, 59.19; H, 3.14; N, 6.28. Found: C, 59.19; H, 3.16; N, 6.27.

Methyl (*E*)-2-cyano-3-(3,5-difluorophenyl)-2-propenoate. Yield 72.2%; m.p. 116°C; ^{1}H NMR δ 3.9 (s, 3H, -OCH_3), 7.0-7.6 (m, Ph-H), 8.2 (s, 1H, CH=); ^{13}C NMR δ 166 (C=O), 163 (CH=), 161, 153, 134, 113 (Ph), 114 (CN), 106 (CH=), 54 (-CH_3); IR (NaCl) 3020 (m, C-H), 2244 (m,C≡N), 1718 (s, C=O), 1250 (s, C-O-CH3), 867 (s, C-H out of plane), 1519 (s, C=C). Anal. Calcd for $C_{11}H_7F_2NO_2$: C, 59.19; H, 3.14; N,6.28. Found: C, 59.28; H, 3.30; N, 6.36.

Methyl (*E*)-2-cyano-3-(2-chloro-6-fluorophenyl)-2-propenoate. Yield 53%; m.p. 94°C; ^{1}H NMR δ 3.9 (s, 3H, -OCH_3), 7.1-7.5 (m, 3H, Ph-H), 8.2 (s, 1H, CH=); ^{13}C NMR δ 165 (C=O), 157 (CH=), 146, 134, 133, 130, 128, 123 (Ph), 115 (CN), 112 (C=) 54 (CH_3); IR (NaCl) 3020 (m, C-H), 2229 (m, C≡N), 1742 (s, C=O), 1209 (s, C-O-CH3), 780 (s, C-H out of plane), 1519 (s, C=C). Anal. Calcd for $C_{11}H_7ClFNO_2$: C, 55.23; H, 2.92; N, 5.86. Found: C, 55.76; H, 3.06; N, 5.96.

Copolymerization

Styrene (ST) (Aldrich) was purified by washing with aqueous sodium hydroxide, drying and subsequent 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 r.t. Copolymers of the TSE monomers and ST were prepared in 25-mL Pyrex screw cap ampoules at an equimolar ratio of the monomer feed using 0.0045 mol/L of AIBN at an overall monomer concentration 2 mole/L in 20 mL of ethyl acetate. The copolymerization was conducted at 80°C. The mixture was cooled to r.t. after 6 hrs and precipitated dropwise in methanol with stirring. 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 with precision of 0.1 wt%.

Results and discussion

Monomer Synthesis

TSE monomers were synthesized by Knoevenagel condensation [6] of a ring-substituted benzaldehyde with an active hydrogen compound, methyl cyanoacetate, catalyzed by a base, piperidine, $R_2C_6H_3CHO$ + $NCCH_2CO_2CH_3$ ---> $R_2C_6H_3CH{=}C(CN)CO_2CH_3$. 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 phenyl group, which is consistent with the NMR data on a variety of substituted 2-cyano-3-phenyl-2-propenoates [7,8].

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. 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 minutes.

Copolymerization

Copolymerization of the methyl 2-cyano-3-dihalophenyl-2-propenoates with ST resulted in formation of copolymers (Table 1) with a number-average molecular weight of $2.9\text{x}10^4$ to $1.39\ \text{x}10^5$ daltons.

Table 1. Copolymerization of styrene (M_1) and methyl 2-cyano-3-dihalophenyl-2-propenoates (M_2), $R_2C_6H_3CH{=}C(CN)CO_2CH_3$.

M_2	Yield, wt%	Nitrogen[a], wt %	m_2, mol % in copolymer	$1/r_1$	MW $\text{x}10^{-3}$	PDI	Tg, °C
24DF	6.3	3.49	36.80	1.40	147.3	2.3	233
25DF	12.3	3.72	40.45	2.11	39.9	1.6	272
26DF	10.1	3.69	39.40	1.84	49.1	2.9	280
34DF	9.4	2.87	29.30	0.65	139.3	1.8	248
35DF	6.7	3.52	37.34	1.71	38.3	1.9	232
2C6F	7.2	2.70	27.80	0.56	29.1	1.8	248

[a] Nitrogen content in the copolymer was determined by elemental analysis.

According to elemental analysis of the copolymers, a substantial amount of TSE 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],

$$m_1/m_2 = [M_1](r_1[M_1] + [M_2])/[M_2]([M_1] + r_2[M_2]) \qquad \text{(I)}$$

m_1 and m_2 are mole fractions of ST and TSE monomer units in the copolymer, respectively; $[M_1]$ and $[M_2]$ are the concentrations of ST and TSE in the monomer feed, respectively. In the absence of self-propagation of the TSE monomer, ($k_{22} = 0$, r_2

= 0) and at equimolar monomer feed ($[M_1/[M_2] = 1$), eq. I yields

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

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

$$1/r_1 = 1/[(m_1/m_2) - 1] \qquad \text{(III)}$$

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 [1]. The order of reactivity ($1/r_1$) for the TSE monomers is 25DF (2.11) > 26DF (1.84) > 35DF (1.71) > 24DF (1.4) > 34DF (0.65) > 2C6F (0.59). The differences in reactivities of the monomers are not significant enough to correlate ring substitution pattern and relative reactivity.

In general, the reactivity of a monomer in a copolymerization reaction depends on: (i) the polarity of the double bond; (ii) the stability of the free radical formed by addition of a growing chain to the monomer; and (iii) steric hindrance in the transition state [1]. Styrene has a high electron-availability at the double bond as measured by its *e*-value of 0.80. The benzyl radical is highly stabilized by resonance with the phenyl ring. The addition of a growing chain end to styrene should not be affected by the presence of the bulky phenyl group because the normal direction of attack on the styrene monomer is toward the ß-carbon to which only two hydrogen atoms are attached. 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. In the ring-dihalogenated TSE monomers, electron-withdrawing halogens increase the positive charge on the double bond. All, except for 34DF and 2C6F, of the ring-substituted monomers were more reactive than the ring-unsubstituted methyl 2-cyano-3-phenyl-2-propenoate with $1/r_1 = 1.3$ [9]. In an attempt to correlate relative reactivity, $1/r_1$ with polarity of the TSE double bond, we have calculated the charge distribution on the olefinic carbons by using HYPERCHEM software. The order of the atomic charges calculated at the planar optimized geometries (AM1) for C_α ($=C(CN)CO_2CH_3$), 35DF (-0.061) < 24DF (-0.034) < 34DF (-0.027) < 25DF (-0.023) < 26DF (-0.006) < 2C6F (-0.01), and $C_ß$ ($R_2PhC=$), 35DF (0.043) > 24DF (0.037) > 34DF (0.031) > 25DF (0.027) > 26DF (0.018) > 2C6F (0.011); C_α and $C_ß$ for unsubstituted methyl 2-cyano-3-phenyl-2-propenoates were -0.080 and 0.027, respectively. The relative reactivity, $1/r_1$, correlates reasonably well with the charges on both olefinic carbons, C_α and $C_ß$. The influence of the substitution on the stability of the free radical is not obvious since apparently the attack of a styrene-ended polymer radical on both sides of the TSE monomer is possible. Thus, Borberly [9] 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.

The structure of the 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 TSE monomer unit are 2235 (w, CN), 1742 (s, C=O), and 1236 cm^{-1} (m, C-O). Benzene rings of both monomers show ring stretching bands at 1492 and 1455 cm^{-1}, as well as a doublet 760, 690 cm^{-1}, associated with C-H out of plane deformations. These bands can be readily identified in styrene copolymers with TSE monomers containing cyano and carbonyl electron withdrawing groups. ^{1}H NMR spectra of the ST-TSE copolymers show a broad double peak in a 6.0-8.0 ppm region corresponding to phenyl ring protons. A peak at 4.2-3.9 ppm is assigned to the methoxy group. A broad resonance at 3.8-2.2 ppm is assigned to the methine proton of the TSE and methine and methylene protons of ST monomer unit close to the propenoate unit, which are more subjected to deshielding than the ones in polystyrene. A double resonance peak in 0.8-2.2 ppm range is attributed to methine and methylene protons of styrene monomer sequences. The ^{13}C NMR spectra also support the suggested skeletal structure of the copolymers. Thus, the assignment of the peaks as follows: 163-168 ppm (C=O), 134-155 ppm (quarternary carbons of both phenyls), 120-145 ppm (phenyl carbons), 110-120 ppm (CN), 50-60 ppm (methine, quarternary and methoxy carbons of the TSE monomers), 45-47 ppm (ST methine) and 40-43 ppm (ST methylene). The broad carbon resonances are most likely due to presence of both head-to-tail and head-to-head dyads. 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, $CHCl_3$ and insoluble in methanol, heptane, and petroleum ether. They are amorphous and show no crystalline DSC endotherm. High T_g of the copolymers (Table 1) in comparison with that of polystyrene (T_g = 95°C) indicates substantial decrease in 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 300-400°C range.

Conclusions

Novel copolymers of electrophilic trisubstituted methyl 2-cyano-3-dihalophenyl-2-propenoates and styrene were prepared by radical copolymerization at equimolar monomer feed. The composition of the copolymers was calculated from nitrogen analysis and the structure was analyzed by IR, ^{1}H and ^{13}C NMR. The order of relative reactivity ($1/r_1$) for the TSE monomers is 25DF (2.11) > 26DF (1.84) > 35DF (1.71) > 24DF (1.4) > 34DF (0.65) > 2C6F (0.59). High T_g of the copolymers indicates substantial decrease in chain mobility of the copolymer due to the high dipolar character of the TSE structural units. The thermal gravimetric analysis indicated that the copolymers decompose in 300-400°C range.

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