

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Novel Copolymers of Styrene and Alkoxy Ring-Disubstituted 2-Phenyl-1,1-dicyanoethylenes

Gregory B. Kharas^a; Selena M. Russell^a; Hope Baird^a; Gerald Cipolla^a; Peter Farina^a; Vikie Fletcher^a; Michel Goizman^a; Kenneth Watson^b

^a Chemistry Department, DePaul University, Illinois, USA ^b Lanxess Inc., Sarnia, Ontario, Canada

To cite this Article Kharas, Gregory B. , Russell, Selena M. , Baird, Hope , Cipolla, Gerald , Farina, Peter , Fletcher, Vikie , Goizman, Michel and Watson, Kenneth(2008) 'Novel Copolymers of Styrene and Alkoxy Ring-Disubstituted 2-Phenyl-1,1-dicyanoethylenes', Journal of Macromolecular Science, Part A, 45: 1, 1 – 4

To link to this Article: DOI: 10.1080/10601320701681797

URL: <http://dx.doi.org/10.1080/10601320701681797>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Novel Copolymers of Styrene and Alkoxy Ring-Disubstituted 2-Phenyl-1,1-dicyanoethylenes

GREGORY B. KHARAS,¹ SELENA M. RUSSELL,¹ HOPE BAIRD,¹ GERALD CIPOLLA,¹ PETER FARINA,¹ VIKIE FLETCHER,¹ MICHEL GOIZMAN,¹ and KENNETH WATSON²

¹Chemistry Department, DePaul University, Illinois, USA

²Lanxess Inc., Sarnia, Ontario, Canada

Received and accepted July, 2007

Electrophilic trisubstituted ethylene monomers, ring-disubstituted 2-phenyl-1,1-dicyanoethylenes, $\text{RC}_6\text{H}_3\text{CH}=\text{C}(\text{CN})_2$ (where R is 2,3-dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 3,4-dimethoxy, 3-ethyl-4-methoxy), were synthesized by piperidine catalyzed Knoevenagel condensation of ring-disubstituted benzaldehydes and malononitrile, and characterized by CHN elemental analysis, IR, ¹H- and ¹³C-NMR. Novel copolymers of the ethylenes and styrene were prepared at equimolar monomer feed composition by solution copolymerization in the presence of a radical initiator (AIBN) at 70°C. The composition of the copolymers was calculated from nitrogen analysis, and the structures were analyzed by IR, ¹H and ¹³C NMR, GPC, DSC, and TGA. High T_g 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 ethylene monomer unit. The gravimetric analysis indicated that the copolymers decompose in the 290–450°C range.

Keywords: trisubstituted ethylenes; radical copolymerization; styrene copolymers

1 Introduction

Previous studies showed that trisubstituted ethylenes containing substituents larger than fluorine have very low reactivity in radical homopolymerization due to polar and steric reasons. 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 (1). Copolymerization of trisubstituted ethylenes (TSE, $\text{CHR}^1=\text{CR}^2\text{R}^3$) 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) show a tendency toward the formation of alternating copolymers.

In continuation of our studies of the monomer structure-reactivity correlation in the radical copolymerization of TSE monomers (4–7), we have prepared alkoxy ring-disubstituted 2-phenyl-1,1-dicyanoethylenes, $\text{RC}_6\text{H}_3\text{CH}=\text{C}(\text{CN})_2$ (where R is 2,3-dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 3,4-dimethoxy, 3-ethyl-4-methoxy), and explore the feasibility of their copolymerization with styrene (ST).

2 Experimental

2.1 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 and the glass transition temperatures (T_g), of the copolymers were measured by using a Polymer Laboratories model DSC STA 625. Thermal stability of the copolymers was measured by using a TA Instruments model TGA 2090. 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 ultrastraygel column and Millenium software. ¹H and ¹³C-NMR spectra of 4–10% CDCl_3 solutions of monomers and polymers were obtained on a Bruker Omega AC-200 spectrometer. Elemental analyses were performed by Quantitative Technologies Inc., NJ.

2.2 Synthesis of Monomers

2.2.1 Monomer Synthesis

The TSE monomers were synthesized by Knoevenagel condensation (8) of a ring-disubstituted benzaldehyde with

Address correspondence to: Gregory B. Kharas, Chemistry Department, DePaul University, IL 60614-3214, USA. Fax: 773-325-7421; E-mail: gkharas@depaul.edu

malononitrile, catalyzed by base, piperidine.



2,3-Dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 3,4-dimethoxy, and 3-ethyl-4-methoxybenzaldehyde, malononitrile, 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 malononitrile and an appropriate ring-disubstituted 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 crystallization from 2-propanol. The condensation reaction proceeded smoothly, yielding crystalline products, which were purified by conventional techniques.

2-(2,3-Dimethoxyphenyl)-1,1-dicyanoethene. Yield 94%; mp 102°C; $^1\text{H-NMR}$ δ 8.3 (s, 1H, CH=), 7.5–6.9 (m, 3H, Ph), 3.8 (s, 6H, OCH₃); $^{13}\text{C-NMR}$ δ 154 (HC=), 81 (>C=), 159, 164 (O-Ph), 130, 106, 107, 98 (Ph), 113 (CN), 56, 60 (OCH₃); IR 3432 (Ar-H stretch), 3053 (C=CH), 2223 (CN), 1603, 1429 (Ar C=C), 748 (o-Ar); Anal. Calc. for C₁₂H₁₀N₂O₂: C 67.28%, H 4.71%, N 13.08%; Found: C 67.20%, H 4.56%, N 13.14%.

2-(2,4-Dimethoxyphenyl)-1,1-dicyanoethene. Yield 81.2%; mp 142°C; $^1\text{H-NMR}$ δ 7.7 (s, 1H, CH=), 7.5–7.2 (m, 3H, Ph), 3.9 (s, 6H, OCH₃); $^{13}\text{C-NMR}$ δ 155 (HC=), 75 (>C=), 159, 164 (O-Ph), 130, 106, 107, 98 (Ph), 113 (CN), 55, 56 (OCH₃); IR 3029 (Ar-H stretch), 3441 (C=CH), 2211 (CN), 1602 (Ar C=C); Anal. Calc. for C₁₂H₁₀N₂O₂: C 67.28%, H 4.71%, N 13.08%; Found: C 67.08%, H 4.41%, N 12.98%.

2-(2,5-Dimethoxyphenyl)-1,1-dicyanoethene. Yield 78%; mp 108°C; $^1\text{H-NMR}$ δ 7.7 (s, 1H, CH=), 7.9, 7.0 (m, 3H, Ph), 3.9 (s, 6H, OCH₃); $^{13}\text{C-NMR}$ δ 153 (HC=), 81 (>C=), 151, 154 (O-Ph), 121, 118, 113, 112 (Ph), 113 (CN), 55, 56 (OCH₃); IR 3435 (Ar-H stretch), 3021 (C=CH), 2220 (CN), 1600, 1421 (Ar C=C), 835 (Ph); Anal. Calc. for C₁₂H₁₀N₂O₂: C 67.28%, H 4.71%, N 13.08%; Found: C 67.10%, H 4.49%, N 13.06%.

2-(3,4-Dimethoxyphenyl)-1,1-dicyanoethene. Yield 83%; mp 146°C; $^1\text{H-NMR}$ δ 7.6 (s, 1H, CH=), 7.9, 7.0 (m, 3H, Ph), 3.8 (OCH₃); $^{13}\text{C-NMR}$ δ 160 (HC=), 77 (>C=), 149, 154 (O-Ph), 128, 124, 112 (Ph), 114 (CN), 56 (OCH₃); IR 3013 (C=CH), 2217 (CN), 1608 (Ar C=C), 820 (p-aromatic); Anal. Calc. for C₁₂H₁₀N₂O₂: C 67.28%, H 4.71%, N 13.08%; Found: C 67.06%, H 4.32%, N 13.13%.

2-(3-Ethyl-4-methoxyphenyl)-1,1-dicyanoethene. Yield 93%; mp 142°C; $^1\text{H-NMR}$ δ 7.6 (s, 1H, CH=), 7.9, 7.0 (m, 3H, Ph), 3.8 (s, 3H, OCH₃), 2.6 (q, 2H, CH₂), 1.2 (t, 3H, CH₃); $^{13}\text{C-NMR}$ δ 160 (HC=), 77 (>C=), 160 (O-Ph), 114, 115, 128, 126 (Ph), 113 (CN), 56 (OCH₃), 23 (CH₂), 14 (CH₃); IR 3426 (C=CH), 2228 (CN), 1609, 1400

(Ar C=C), 830 (Ar); Anal. Calc. for C₁₃H₁₂N₂O: C 73.57%, H 5.70%, N 13.20%; Found: C 73.12%, H 5.83%, N 12.63%.

2.3 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 ambient temperature. Copolymers of the TSE and ST were prepared in 50-ml Pyrex screw-cap ampoules at an equimolar ratio of the monomer feed using 0.0045 mole/l of AIBN at an overall monomer concentration 2 mole/l in ethyl acetate (total volume 20 ml). The copolymerization was conducted at 70°C. After a predetermined time, the mixture was cooled to ambient temperature and precipitated dropwise in methanol. The crude copolymers were purified by reprecipitation from solution into an excess of methanol. Then, the copolymers were dried under reduced pressure at 60°C until constant weight. The composition of the copolymers was determined based on the nitrogen content.

3 Results and Discussion

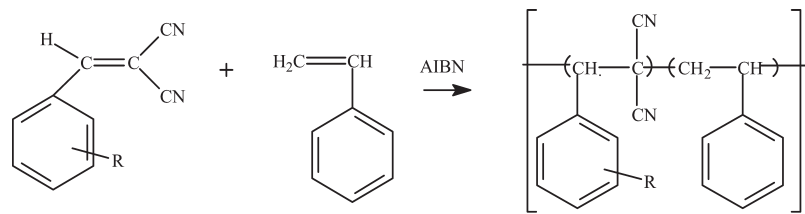
3.1 Homopolymerization

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

3.2 Copolymerization

Copolymerization (Scheme 1) of the alkoxy ring-disubstituted 2-phenyl-1,1-dicyanoethylenes with ST resulted in formation of copolymers (Table 1) with weight-average molecular masses 48.7×10^3 to 80.5×10^3 daltons. According to elemental analysis, a substantial amount of TSE monomer is present in the copolymers, which is indicative of relatively high 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



Sch. 1. ST-TSE copolymer synthesis. R is 2,3-dimethoxy, 2,4-dimethoxy, 2,5-dimethoxy, 3,4-dimethoxy, and 3-ethyl-4-methoxy.

composition equation Equation (1) of the terminal copolymerization model (1).

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

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 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 ($[M_1]/[M_2] = 1$), Equation (1) yields:

$$r_1 = m_1/m_2 - 1 \quad (2)$$

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

$$1/r_1 = 1/(m_1/m_2) - 1 \quad (3)$$

Consideration of monomer reactivities according to Equation (3) involves also the assumption of minimal copolymer compositional drift at equimolar monomer feed and given conversion. This non-rigorous kinetic treatment nevertheless allows estimation of the reactivity of a ST-ended polymer radical in reaction with electrophilic monomer. Thus the order of relative reactivity ($1/r_1$) and the tendency toward alternation of monomer units in the copolymer for the five TSE monomers is 2,3-dimethoxy (4.51) > 2,5-dimethoxy (2.69) > 2,4-dimethoxy (2.06) > 3,4-dimethoxy (0.83) > 3-ethyl-4-methoxy (0.74). 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.

3.3 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 the 3800–2800 cm^{-1} region corresponding to C-H stretching vibrations. The spectra of the copolymers show weak cyano group absorption of the TSE monomer unit at 2230–2248 cm^{-1} (2222–2230 cm^{-1} in the monomer). Benzene rings of both monomers show ring stretching bands at 1497–1520 and 1456–1462 cm^{-1} , as well as a doublet 750–650 cm^{-1} , associated with C-H out of plane deformations. These bands were found also in copolymers of 2-phenyl-1,1-dicyanoethylene with vinyl acetate (9) and *N*-vinyl-2-pyrrolidone (5).

$^1\text{H-NMR}$ spectra of the ST-TSE copolymers show a broad double peak in a 6.2–7.9 ppm region corresponding to phenyl ring protons. The resonance at 3.2–3.8 ppm is assigned to ST backbone protons in the close proximity of in ST-TSE dyad or in ST centered TSE-ST-TSE triads. The low and high field components of the 2.0–2.9 ppm peak is assigned to the overlapping resonances of the methine proton of the TSE monomer unit in head-to-tail and head-to-head structures (10). Alkoxy protons of TSE monomers units have the same chemical shifts as those of the monomers. Backbone ST protons removed further from cyano groups give rise to the absorption in 1.7–2.4 ppm with a maximum at 2.2 ppm. The strong absorption in the 0.7–2.1 ppm range corresponds to ST backbone protons in ST-ST diads. The $^{13}\text{C-NMR}$ spectra also support the suggested skeletal structure of the copolymers. Thus, the assignment of the peaks as follows: 137–147 ppm (quaternary carbons of both phenyls), 120–145 ppm (phenyl carbons), 110–120 ppm (CN),

Table 1. Copolymerization of styrene (M_1) and alkoxy ring-disubstituted 2-phenyl-1,1-dicyanoethylenes, $\text{RC}_6\text{H}_3\text{CH}=\text{C}(\text{CN})_2$ (M_2)

R (M_2)	Yield (wt.%)	Nitrogen (wt.%)	M_2 (mol%)	MW (10^3 daltons)	Tg ($^\circ\text{C}$)	Onset of Decomp. (TGA), $^\circ\text{C}$
2,3-(CH_3O) ₂	32.0	8.21	45.0	50.7	140	303
2,4-(CH_3O) ₂	14.9	7.60	40.2	62.9	152	306
2,5-(CH_3O) ₂	43.0	7.85	42.2	80.5	177	319
3,4-(CH_3O) ₂	9.0	6.32	31.2	48.7	165	311
3- C_2H_5 ,	14.2	6.12	29.8	57.8	158	320
4- CH_3O						

Polymerization time was 8 h.

55–65 ppm (methine carbons of TSE and ST, and ST methylene). The broad carbon resonances are due to presence of both head-to-tail and head-to-head dyads as discussed in more detailed assignment of ^1H and ^{13}C -NMR spectra of 2-phenyl-1,1-dicyanoethylene-ST copolymers (10). The IR and NMR data showed that these are true copolymers, composed of ST and TSE monomer units.

The copolymers prepared in the present work are all soluble in ethyl acetate, DMF, CHCl_3 and insoluble in methanol, ethyl ether, and heptane. They are amorphous and show no crystalline DSC endotherm. High T_g of the copolymers (Table 1) in comparison with that of polystyrene ($T_g = 95^\circ\text{C}$) indicates substantial decrease of chain mobility of the copolymer due to high dipolar character of the structural unit. 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. The decomposition of all copolymers in nitrogen occurs rapidly in one stage in the 300–450°C range.

4 Conclusions

Electrophilic trisubstituted ethylene monomers, alkoxy ring-disubstituted 2-phenyl-1,1-dicyanoethylenes, were prepared via a base-catalyzed condensation of appropriate disubstituted benzaldehydes and malononitrile. The copolymerization of the ethylenes with styrene resulted in statistical copolymers, with the ethylene mole percent in the range 29.8–45.0% (mole). The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, ^1H - and ^{13}C -NMR. High glass transition temperatures of the copolymers, in comparison with that of polystyrene, indicate a substantial decrease in the chain mobility of the copolymers due to the high dipolar character of the trisubstituted ethylene monomer unit. The gravimetric

analysis indicated that the copolymers decompose in the range 290–450°C.

5 Acknowledgments

We are grateful to acknowledge that the project was partly supported by the research and equipment grants from the National Science Foundation's DUE Grant (No. 9455681), Coating Industry Education Fund (CIEF), Chicago Society of Coatings Technology, the DePaul University Research and Quality of Instruction Councils, and Office of Sponsored Programs and Research. SMR was supported by the CIEF graduate fellowship.

6 References

1. Odian, G. *Principles of Polymerization*, 3rd Edn.; Wiley: New York, 1991.
2. Hall, H.K., Jr. and Daly, R.C. (1975) *Macromolecules*, **8**, 22–31.
3. Kharas, G.B. Trisubstituted ethylene copolymers. In *Polymeric Materials Encyclopedia*; Salamone, J.C. (ed.); CRC Press: Boca Raton, FL, 8405–8409, Vol. 11, 1996.
4. Kharas, G.B. (1988) *J. Appl. Polym. Sci.*, **35**, 733–741.
5. Kharas, G.B. (1988) *J. Appl. Polym. Sci.*, **35**, 2173–2181.
6. Kharas, G.B., Karras, J.W., Michna, V.K., Grajzer, K., Karins, K.A., Kontzias, C., Rothacker, E.P., McManigal, K.A., Dian, B.C. and Watson, K. (2001) *J. Macromol. Sci.*, **A38**, 889–896.
7. Kharas, G.B., Smith, D.G., Karras, J.W., Maslanka, M., Mendelsohn, Y., Pintaric, A., Sklovsky, M., Wilder, A. and Watson, K. (2006) *J. Macromol. Sci.*, **43(1)**, 39–44.
8. Smith, M.B. and March, J. Addition to carbon-hetero multiple bonds. In *March's Advanced Organic Chemistry*; J. Wiley & Sons: New York, Ch. 16, 1225, 2001.
9. Kharas, G.B. and Kohn, D.H. (1984) *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 583–588.
10. Kharas, G.B., Murau, P.A., Watson, K. and Harwood, H.J. (1992) *Polym. Int.*, **28**, 67–74.