Synthesis and Analysis of Novel Copolymers of Ring-Substituted 2-Phenyl-1, 1-dicyanoethylenes and Styrene

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Synthesis and Analysis of Novel Copolymers of Ring-Substituted
2-Phenyl-1,1-dicyanoethylenes and Styrene

A Thesis
Presented in
Partial Fulfillment of the
Requirements for the Degree of
Master of Science
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ABSTRACT

Novel copolymers of styrene and trisubstituted ethylene monomers, ring-substituted 2-phenyl-1,1-dicyanoethylenes, \( \text{RC}_6\text{H}_4\text{CH} = \text{C(CN)}_2 \) (where \( R \) is 2-ethyl, 4-isopropyl, 4-butyl, 4-tert-butyl, 4-isobutyl, 2-ethoxy, 4-hexyloxy, and 2-cyano), were prepared by radical copolymerization at 70°C. The monomers were synthesized by Knoevenagel condensation of ring-substituted benzaldehydes with malononitrile, catalyzed by piperidine. 2-Ethyl-substituted monomer was prepared and characterized first time and is not reported in literature. The structures of resulting copolymers were analyzed by IR, \(^1\text{H}-\) and \(^{13}\text{C}-\)NMR spectroscopy. The average molecular weights of the copolymers were determined by gel permeation chromatography. The copolymer compositions were calculated from nitrogen analysis. Structural and compositional analyses show that the resulting polymers are true copolymers. The order of the relative reactivity, ratio of rate constants of cross propagation to that of styrene self-propagation \((1/r_1)\) was estimated as follows, \(4\text{-tert}-\text{butyl} (1.45) > 4\text{-isopropyl} (1.38) > 2\text{-ethyl} (1.37) > 4\text{-hexyloxy} (1.33) > 2\text{-cyano} (1.32) > 4\text{-butyl} (1.04) > 4\text{-isobutyl} (1.02) > 2\text{-ethoxy} (0.63)\). All copolymers have a higher glass transition temperature \((T_g)\) than that of polystyrene, as determined by DSC, indicating a substantial decrease in chain mobility of the copolymers due to the high dipolar character of the trisubstituted monomer unit. Thermal stability studies of the copolymers by thermogravimetric analysis indicated that the copolymers decomposed rapidly in one stage in 200-400 °C range followed by a slower decomposition of the residue at 400-800 °C.

1. INTRODUCTION

Innovative polymers are helping to advance almost every field of material science, ranging from alternative energy to organic electronics to reconstructive surgery. Polymers can have many attractive characteristics, including their light weight, mechanical flexibility, fracture tolerance, high chemical resistance, ease of processing, and low manufacturing cost.

There is a significant interest related to functionalization of polymers. This is the process of introducing chemical groups into a polymer molecule, or converting one chemical group to another to enhance chemical, physical, biological, pharmacological, or other functions. In spite of significant amount of work in the field, we are still far from having a full understanding of the factors that contribute to the performance of polymeric materials. Due to the large diversity of synthetic
polymers, there are extensive research opportunities to correlate the structure and reactivity of monomers to the structure and properties of polymers. Furthermore, the relationships developed from these studies of polymers are particularly important for the design of new polymeric materials for advanced applications.

The polymers explored in this research project belong to the pendant-functionalized type, which have functional groups as side groups on the polymer chain. Many functional polymers are based on commercial monomers and polymers like styrene, vinyl acetate, polyolefins, dienes, etc. One of the most common methods used to introduce functional groups into a macromolecule is radical copolymerization which allows relative control of functional group composition and distribution along the chain.

The ability to control functional group placement and polymer backbone structure in synthetic polymers is essential for understanding fundamental structure-property relationships as well as designing polymeric materials with important performance characteristics. New, precisely functionalized polymers, which are based on easily scaleable and industrially practiced free-radical polymerization chemistries, have significant potential to have practical impact across a broad range of advanced technology frontiers.

Motivated by the desire to create novel polymeric structures, that could serve as a spring board for further development of novel polymeric materials with new properties and applications, the polymer research group in the chemistry department continues to study the synthesis of a series of novel functional electrophilic trisubstituted ethylenes (TSEs), ring substituted \(R^{1} \text{PhCH=CR}^{2} \text{R}^{3}\) (where \(R^{1}\) is a diverse family of substituents, versus \(R^{2}\) and \(R^{3}\), which are electron-withdrawing substituents). The TSE monomers do not form homopolymers via radical initiation due to steric hindrance but readily form alternating copolymers with styrenic monomers, vinyl acetate, vinyl ethers, and other electrophilic alkenes.

Trisubstituted ethylenes continue to attract attention of polymer chemists as reactive comonomers and models for mechanistic studies. It was shown that electrophilic tri- and tetra substituted olefins are particularly useful in delineating the transition from radical chemistry to ionic chemistry [1].
Previous studies showed that TSE 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 tetra substituted olefins, their copolymerization with a monosubstituted alkene makes it possible to overcome these steric problems [2]. Copolymerization of TSE having double bonds substituted with halo, cyano, and carbonyl groups and electron-rich monosubstituted ethylenes such as styrene, N-vinylcarbazole, and vinyl acetate [3-5] show a tendency toward the formation of alternating copolymers. Ring–unsubstituted 2-phenyl-1,1-dicyanoethylene was copolymerized with styrene [6], vinyl ethers [7], methyl methacrylate [8], and N-vinyl-2-pyrrolidone [9].

In relation to applications, piezoelectric activity was observed in a copolymer of 1,1-dicyanoethylene (vinyledene cyanide) and vinyl acetate [10]. Unlike fluoropolymers, this copolymer is amorphous with high Tg of 178 °C and has an alternating monomer unit structure. The copolymer has impedance similar to that of the human body and has been suggested for medical applications as an ultrasonic transducer [11]. When a high electric field is imposed to the copolymer film near its glass transition temperature, a thin fiber-like assembly about 10 nm thick appears on the surface [12]. This behavior in electric field (piezoelectric and dielectric) has been attributed to a strong dipole moment of nitrile groups and the presence of free volume which is able to abate electrostatic interactions between vinyl acetate dipoles and facilitating orientation of these dipoles in the direction of the applied field [13].

In continuation of the research on styrene copolymerization with TSE monomers, it was of interest to study radical copolymerization of ring-substituted 2-phenyl-1, 1-dicyanoethylene, \( \text{RC}_6\text{H}_4\text{CH} = \text{C(CN)}_2 \) and styrene. Varying the identity and position of the substituent on the ring yields a broad range of additional functionality to the copolymer chain. For this particular thesis, eight groups (2-ethyl, 4-isopropyl, 4-butyl, 4-isobutyl, 4-tert-butyl, 2-ethoxy, 4-hexyloxy, and 2-cyano) were chosen for the ring substitution. The feasibility of copolymerization of these monomers for with styrene was studied for the first time.

The specific objectives of this study were to:

1) Prepare and confirm the structure of the ring-substituted 2-phenyl-1, 1-dicyanoethylenes
2) Explore the feasibility of their copolymerization with styrene
3) Characterize composition, structure, and molecular weight of the copolymers
4) Study the copolymers’ thermal behavior
5) Compare relative reactivity of these monomers in propagation reactions.

2. MATERIALS AND METHODS

2.1 Materials

2-ethyl, 4-isopropyl, 4-butyl, 4-isobutyl, 4-tert-butyl, 2-ethoxy, 4-hexyloxy, 2-cyano benzaldehydes, malononitrile, and piperidine were used for TSE monomer synthesis. 2-propanol was used for TSE monomer purification via recrystallization. Styrene, toluene, 1,1’-azobis (cyclohexanecarbonitrile) (ABCN), methanol, and petroleum ether were used for TSE copolymerization. Dichloromethane, tetrahydrofuran (THF), and chloroform-d (99.8 atom % D) were used for analysis of TSE monomers and copolymers. All the materials were purchased from Aldrich and used as received.

2.2 General Analysis Procedures

The melting points of the monomers and the glass transition temperature ($T_g$) of the copolymers were measured with a differential scanning calorimeter: TA instruments DSC Q10. The thermal scans were performed in the 40-250°C range at a heating rate of 15 °C/min in aluminum pans. $T_g$ was determined by taking the midpoint of a straight line between the inflection of the peak’s onset and endpoint. The thermal stability of the copolymers was measured by thermogravimetric analysis using TA instruments TGA Q50. The thermal scans were performed from ambient temperature up to 800°C at a heating rate of 20°C/min using platinum pans. Infrared spectra of the TSE monomers and copolymers were determined with a Nicolet Avatar 360 FT-IR spectrometer, using KBr plates. The molecular weights of the copolymers were determined relative to polystyrene standards in THF solutions with sample concentrations of 0.8 % (w/v) by gel permeation chromatography (GPC) using HPLC Pump Model 426 by Altech at an elution rate of 0.6 mL/min, coupled with a Phenogel 5m Linear column at 25°C, Viscotek TDA (Triple Detector Array) 302 and Viscotek Model 2501 UV detector. $^1$H- and $^{13}$C-NMR spectra were obtained on 10-25% (w/v) monomer or copolymer solutions in CDCl$_3$ at ambient temperature, using Bruker Avance 300 MHz spectrometer. Elemental analyses were performed by Quantitative Technologies Inc. (New Jersey). CHN wt% of monomers was used to confirm monomer
purity and N wt% of copolymers was used to determine the monomer composition.

3. RESULTS AND DISCUSSION

3.1 Synthesis of Monomers

The TSE monomers were synthesized by Knoevenagel condensation [7] of a ring-substituted benzaldehyde with malononitrile catalyzed by a base, piperidine (Figure 1):

![Figure 1. TSE Monomer Synthesis](where R = 2-ethyl, 4-isopropyl, 4-butyl, 4-tert-butyl, 4-isobutyl, 2-ethoxy, 4-hexyloxy, 2-cyano)

Mechanism of TSE monomer synthesis is presented in Figure 1a.

![Figure 1a. TSE Monomer Synthesis Mechanism](where R = 2-ethyl, 4-isopropyl, 4-butyl, 4-tert-butyl, 4-isobutyl, 2-ethoxy, 4-hexyloxy, 2-cyano)
All the TSE monomers were synthesized by following the same preparation procedure; equimolar amounts of malononitrile and the appropriate ring-substituted benzaldehyde were mixed in a reaction vial. The mixture was occasionally heated in a warm water bath (~40°C) to melt some aldehydes and malononitrile. A few drops of piperidine were added with stirring. The condensation reaction proceeded smoothly at room temperature, yielding crystalline monomers. The crystalline products of the reaction were isolated by filtration and purified by recrystallization from 2-propanol.

The purified products were dried in a vacuum oven at room temperature and the crystalline products were analyzed by DSC, IR, $^1$H- and $^{13}$C-NMR spectroscopy (Attachments 1-4), and CHN elemental analysis. The characterization results for the prepared monomers are below. Except 2-Ethyl, all other monomers were prepared in the past for copolymerization with vinyl acetate and 4-fluorostyrene.

3.1.1. 2-(2-Ethylphenyl)-1,1-dicyanoethylene
Yield: 67%; mp 73°C; $^1$H-NMR δ 1.18 (t, 3H, CH$_3$), 2.85 (q, 2H,CH$_2$), 7.21 (d, 1H,phenyl), 7.24(t, 2H, phenyl), 7.79(d, 1H, phenyl), 7.83 (s, 1H, CH) ; $^{13}$C-NMR δ 16.20 (CH$_3$), 26.77 (CH$_2$), 114, 112.62 (CN), 134.48, 130.01, 129.28, 128.68, 127.19 (phenyl), 158.49(CH=), 146.08 (=C<); IR (cm$^{-1}$) 2973 (m, C-H phenyl), 2228 (s, CN), 763, 804 (m, C-H out-of-plane bending). Anal. Calcd.: C, 79.1%; H, 5.53 %; N, 15.437%; Found: C, 79.59%; H, 5.77%; N, 15.42%.

3.1.2. 2-(4-Isopropylphenyl)-1,1-dicyanoethylene
Yield: 34%; mp 42°C; $^1$H NMR δ 1.22 (d, 6H, CH$_3$), 2.88 (sep, 1H, CH), 7.69(s, 1H, CH=), 7.26,7.87 (d, 4H,phenyl); $^{13}$C-NMR δ 23 (CH$_3$), 115 (C<), 113 (CN), 129, 130, 132 (phenyl), 159 (CH=); IR (cm$^{-1}$) 3033, 2964 (m, C-H phenyl), 2228 (s, CN), 1588 (s, C=C), 834, 615 (m, C-H out-of-plane bending). Anal. Calcd.: C, 79.54%; H, 6.179%; N, 14.3%; Found: C, 78.03%; H, 6.18%; N, 14.44%.

3.1.3. 2-(4-Butylphenyl)-1,1-dicyanoethylene
Yield: 98%; mp 122°C; $^1$H NMR δ 0.90 (t, 3H, CH$_3$), 1.3, 1.5 (m, 4H, CH$_2$), 2.6 (m, 2H, CH$_2$), 7.4
(m, 2H, phenyl), 7.8 (d, 2H, phenyl), 7.7 (d, 1H, CH=); $^{13}$C-NMR δ 14 (CH$_3$), 22.58, 22.44, 33.15, 36.09 (CH$_2$), 117(=C<), 113 (CN), 129.88, 131.13, 128 (phenyl), 159.99 (CH=); IR (cm$^{-1}$) 2956, 2930 (m, C-H phenyl), 2228 (s, CN), 1600 (s, C=C), 833 (m, C-H out-of-plane bending). Anal. Calcd: C, 79.9%; H, 6.7%; N, 13.3%; Found: C, 79.2%; H, 6.65%; N, 13.32%.

3.1.4. 2-(4-Isobutylphenyl)-1,1-dicyanoethylene

Yield: 51%; mp 81°C; $^1$H NMR δ 0.91 (d, 6H, CH$_3$), 1.84 (sep, 1H, CH), 2.44 (d, 2H,CH$_2$),7.32,7.87 (d, 4H, phenyl), 7.69 (s, CH=); $^{13}$C NMR δ 22.48 (CH$_3$), 31.09, 30.31 (CH), 45.77 (CH$_2$), 131.01, 130.56, 128.91 (phenyl), 113 (CN), 117 (=C<), 159.97 (CH=); IR (cm$^{-1}$) 3432.2, 2959.8, 2907.8, 2855.9 (w, C-H phenyl), 2232.3 (s, CN), 1589.8 (s, C=C), 848.1 (s, C-H out-of-plane bending). Anal. Calcd: C, 79.97%; H, 6.71%; N, 13.32%; Found: C, 79.2%; H, 6.65%; N, 13.32%.

3.1.5. 2-(4-tert-Butylphenyl)-1,1-dicyanoethylene

Yield: 116%; mp 98°C; $^1$H-NMR δ 1.34 (s, 9H, CH$_3$), 7.69 (s, 1H, CH=), 7.43 (d, 2H, phenyl),7.87 (d, 2H, phenyl); $^{13}$C-NMR δ 31.11, 31.08 (CH$_3$), 113 (CN), 117 (=C<), 131.05, 126.88, 128 (phenyl), 159.99 (CH=); IR (cm$^{-1}$) 3034, 2965 (w, C-H phenyl), 2240 (s, CN), 1555, 1588 (s, C=C), 835, 778 (m, C-H out-of-plane bending). Anal. Calcd: C, 79.96%; H, 6.71%; N, 13.33%; Found: C, 79.43%; H, 6.53%; N, 13.22%.

3.1.6. 2-(2-Ethoxyphenyl)-1,1-dicyanoethylene

Yield 81%; mp 89°C; $^1$H-NMR δ 1.5 (t, 3H, OCH$_2$CH$_3$), 4.2 (q, 2H,OCH$_2$CH$_3$), 8.4 (s, 1H, CH=), 6.98,7.22,7.25,7.44 (m, 4H, phenyl); $^{13}$C-NMR δ 14.64 (OCH$_2$CH$_3$), 64.64 (OCH$_2$CH$_3$),113 (CN), 81(=C<), 112.24, 121.02, 128.84, 136.50 (phenyl), 154.63 (CH=); IR (cm$^{-1}$) 2991 (m, C-H phenyl), 2226 (s, CN), 1599, 1583 (s, C=C), 747, 614 (m, C-H out-of-plane bending), 1259 (s, C-O ether); Anal. Calcd: C, 72.71%; H, 5.08%; N, 14.13%; Found: C, 72.23%; H, 4.59%; N, 14.14%.
3.1.7. 2-(4-Hexyloxyphenyl)-1,1-dicyanoethylene

Yield 59%; mp 64°C; $^1$H-NMR $\delta$ 0.90 (t, 3H, CH$_3$), 7.7 (s, 1H, CH=), 1.25,1.37,1.51, 1.83 (m, 8H, CH$_2$), 4.03(t, 2H, OCH$_2$), 7.0(d,2H, phenyl), 7.49 (d, 2H, phenyl); $^{13}$C-NMR $\delta$ 14 (CH$_3$), 22 ,29, 31.75, 31.21 (CH$_2$), 113 (CN), 77.33 (=C<), 115.82, 122, 133.78, 164 (Ph), 159 (=CH); IR (cm$^{-1}$) 2937 (w, C-H phenyl), 2223 (s, CN), 1517,1580,1561 (s, C=C), 831,723 (m, C-H out-of-plane bending), 1277 (s, C-O ether) ; Anal. Calcd: C, 75.5%; H, 7.1%; N, 11%; Found: C, 75.38%; H, 6.82%; N, 11.02%.

3.1.8. 2-(2-Cyanophenyl)-1,1-dicyanoethylene

Yield 25%; mp 102°C; $^1$H-NMR $\delta$7.67,7.79 (m, 2H, phenyl), 8.2 (s, 1H, CH=), 7.24 (m, 2H, phenyl); $^{13}$C-NMR $\delta$ 113 (CN), 114.66 (=C<), 134.05, 133.94, 133.67, 132.78, 128.70 (phenyl), 154.54 (CH=); IR (cm$^{-1}$) 2900 (s, C-H phenyl), 2215 (s, CN), 1702, 1599,1581 (s, C=C), 763 (C-H out-of-plane bending); Anal. Calcd: C, 73.74%; H, 2.82%; N, 23.46%; Found: C, 72.80 %; H, 2.79 %; N, 22.70%

The analyses of the TSE monomers above are consistent with previous literature data [8]. All the spectra showed predicted peaks, indicating the desired structures of monomers. The chemical compositions of monomers were consistent with the theoretical values (discrepancy < 5 %) supporting the suggested structures of monomers as well as the purity of monomers. Except for 2-(2-Ethylphenyl)-1,1-dicyanoethylene, all other monomers have been prepared earlier with discrepancy < 5% and have been reported to have successfully formed the desirable copolymers [5-6,8]. In other words, the purity of the monomers formed is good for producing copolymers.

3.2 Homopolymerization

An attempted homopolymerization of the TSE monomers in the presence of 1,1'-Azobis(cyclohexanecarbonitrile) (also known as ABCN) did not produce any polymer as indicated by the lack of a precipitate in methanol and petroleum ether. Inability of the monomers to polymerize is associated with steric crowding encountered in homopolymerization of 1,1- and 1,2-disubstituted ethylenes. Increasing reaction time or amount of radical initiator did not solve this problem. 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 styrene (ST) under conditions identical to those in the copolymerization experiments yielded 18.3% of polystyrene, when polymerized for 30 minutes [9]. TSE doesn’t homopolymerize and only ST does. Hence here we do not compare the yield obtained from homopolymerization of ST or the time needed for homopolymerization of ST with that of copolymerization of ST and TSE.

3.3 Copolymerization

ST-TSE copolymers were synthesized by radically initiated addition polymerization (Figure 2). The reaction and reaction mechanism are shown below:

![Figure 2. ST-TSE Copolymerization Reaction](image-url)
Mechanism:

RADICAL CLEAVAGE

\[ \text{Figure 2a. Radical Cleavage and Radical Initiation} \]

RADICAL INITIATION

\[ \text{Figure 2b. Radical Propagation and Chain Termination} \]
Each copolymerization reaction mixture was prepared in a 25-mL glass screw cap vial at ST/TSE = 3/1 molar ratio of the monomer feed. 0.12M of ABCN was added at an overall monomer concentration of 3.5M in 10 g of toluene. The copolymerization was conducted at 70°C for 8 hours. The reaction mixture was precipitated by drop-wise addition into an excess amount of methanol with stirring. The crystalline products were isolated by vacuum filtration and dried for analyses.

3.3.1 Results of Copolymerization

Copolymerization of styrene and the ring-substituted 2-phenyl-1,1-dicyanoethylenes resulted in formation of copolymers (Table 1). At the comonomer feed ST/TSE = 3/1 (mol) the mole fraction of TSE in the copolymer varies from 0.10 to 0.25.

Table 1. Copolymerization of styrene (M\(_1\)) and ring-substituted 2-phenyl-1,1-dicyanoethylenes, \(\text{RC}_6\text{H}_4\text{CH}=\text{C(CN)}_2\) (M\(_2\))

<table>
<thead>
<tr>
<th>R</th>
<th>yield, wt%</th>
<th>N, wt%</th>
<th>(\text{mol fraction of TSE (m}_2)</th>
<th>(r_l=(m_1/m_2-1)/3) and (r_l=(m_1/m_2-1)/10) for 2-cyano</th>
<th>(1/r_l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-ethyl</td>
<td>45</td>
<td>5.45</td>
<td>0.24</td>
<td>0.73</td>
<td>1.37</td>
</tr>
<tr>
<td>4-isopropyl</td>
<td>52</td>
<td>5.31</td>
<td>0.24</td>
<td>0.73</td>
<td>1.38</td>
</tr>
<tr>
<td>4-butyl</td>
<td>45</td>
<td>4.56</td>
<td>0.20</td>
<td>0.96</td>
<td>1.04</td>
</tr>
<tr>
<td>4-isobutyl</td>
<td>71</td>
<td>4.52</td>
<td>0.20</td>
<td>0.98</td>
<td>1.02</td>
</tr>
<tr>
<td>4-tert-butyl</td>
<td>77</td>
<td>5.29</td>
<td>0.25</td>
<td>0.69</td>
<td>1.45</td>
</tr>
<tr>
<td>2-ethoxy</td>
<td>54</td>
<td>3.51</td>
<td>0.15</td>
<td>1.59</td>
<td>0.63</td>
</tr>
<tr>
<td>4-hexyloxy</td>
<td>76</td>
<td>4.72</td>
<td>0.23</td>
<td>0.75</td>
<td>1.33</td>
</tr>
<tr>
<td>2-cyano</td>
<td>21</td>
<td>3.91</td>
<td>0.10</td>
<td>0.76</td>
<td>1.32</td>
</tr>
</tbody>
</table>

\(^{a)}\) polymerization time was 8 hours
\(^{b)}\) monomer composition (monomer feed) ST/TSE = 3/1 (mol)

Monomer composition refers to the ratio of ST/TSE which is 3/1. \(m_2\) is the content of TSE monomer unit in copolymer. Maximum value for \(m_2\) is 0.25. Value of \(m_2\) ranged from 0.10 to 0.25. This indicates that the ratio of ST/TSE in the copolymer remained similar to their ratio in the monomer feed.

We do not study the conversion with respect to time. It is assumed that \(m_2\) does not change significantly
with time at given ST/TSE composition =3.

3.3.2 Monomer Reactivity

For the copolymerization of TSE monomer with ST monomer, two reactive centers (radical chain ends) are possible: \( \sim \sim \sim \text{ST} \cdot (M_1) \) and \( \sim \sim \sim \text{TSE} \cdot (M_2) \). And the two types of reactive centers lead to four potential propagation reactions as shown below:

<table>
<thead>
<tr>
<th>Radical chain end</th>
<th>Monomer</th>
<th>New radical chain end</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \sim \sim \sim \text{ST} \cdot )</td>
<td>ST</td>
<td>( k_{11} \rightarrow \sim \sim \sim \text{ST-ST} \cdot )</td>
</tr>
<tr>
<td>( \sim \sim \sim \text{ST} \cdot )</td>
<td>TSE</td>
<td>( k_{12} \rightarrow \sim \sim \sim \text{ST-TSE} \cdot )</td>
</tr>
<tr>
<td>( \sim \sim \sim \text{TSE} \cdot )</td>
<td>ST</td>
<td>( k_{21} \rightarrow \sim \sim \sim \text{TSE-ST} \cdot )</td>
</tr>
<tr>
<td>( \sim \sim \sim \text{TSE} \cdot )</td>
<td>TSE</td>
<td>( k_{22} \rightarrow \sim \sim \sim \text{TSE-TSE} \cdot )</td>
</tr>
</tbody>
</table>

\( k_{11}, k_{12}, k_{21}, \) and \( k_{22} \) are reaction constants of self-propagation of ST, cross-propagation of ST to TSE, cross-propagation of TSE to ST, and self-propagation of TSE, respectively.

In an attempt to qualitatively correlate the observed monomer reactivities, the copolymer composition data obtained at 3/1 monomer feed were considered. The reactivity of ST in copolymerization with these monomers can be estimated by assuming applicability of the copolymer composition equation (Equation 1) \[1\]. Rate constants in equation 1 do not depend on time.

\[
m_1/m_2 = \frac{[M_1](r_1[M_1] + [M_2])/([M_1] + r_2[M_2])} {[M_2]} \quad (1).
\]

\( m_1 \) 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; \( r_1 = k_{11}/k_{12} \) and \( r_2 = k_{22}/k_{21} \), the reactivity ratios of self-propagation to cross-propagation. In the absence of the self-propagation of TSE monomers \( (k_{22} = 0 \text{ and thus } r_2 = 0) \) and when we have \( ([M_1]/[M_2] = 3) \) Equation 1 yields.

\[
r_1 = (m_1/m_2 - 1)/3 \quad (2)
\]

or the equation for the relative reactivity of ST radical with trisubstituted ethylene monomers is:

\[
1/r_1 = 3/[(m_1/m_2) - 1] \quad (3)
\]
Consideration of monomer reactivities according to Equation 3 involves also the assumption of minimal copolymer compositional drift at 3/1 monomer feed. Thus, the order of relative reactivity \((1/r_1)\) for the eight TSE monomers is 4-tert-butyl (1.45) > 4-isopropyl (1.38) > 2-ethyl (1.37) > 4-hexyloxy (1.33) > 2-cyano (1.32) > 4-butyl (1.04) > 4-isobutyl (1.02) > 2-ethoxy (0.63). The above reactivities have a very high error due to the kinetic model assumptions. They can serve only as a “ball park” number for the commercial development of these polymers. The attempted correlation of the relative reactivity (data based on a single experiment) to the type of substitutions, the length and/or position of the substituent, failed possibly due to lack of statistically significant number of samples. More detailed information on the copolymer composition, such as stereochemistry of the microstructure at different monomer feed ratios would be necessary for the application of copolymerization models which would allow prediction of reliable copolymer composition. No additional experiments were conducted due to focus of this research on the feasibility studies. This type of correlation could be an objective of a separate study.

According to elemental analysis, the relative reactivity \((1/r_1)\) for most of the copolymers was more than 1. Hence \(k_{12} > k_{11}\) which indicates high reactivity of the monomers in cross-propagation reactions (Table 1).

3.4 Structure and Properties

A comparison between the spectra of the copolymers and polystyrene shows that the reaction between the TSE monomers and ST is a copolymerization.

3.4.1 Structure

The copolymer structure was characterized by IR and NMR spectroscopy.

An example of FTIR spectra of the ST-TSE copolymers is presented in Figure 4.
All the IR spectra of the copolymers show overlapping bands in the 3200-2800 cm\(^{-1}\) region corresponding to C-H vibrations. The spectra of the copolymers show weak cyano group absorption of the TSE monomer unit in 2230-2250 cm\(^{-1}\) region. In the monomer the cyano band had appeared in 2222-2230 cm\(^{-1}\) region with stronger intensity. This indicates that the cyano band in the polymers’ spectra belongs to copolymers instead of unreacted monomer contamination. The band corresponding to carbon of ST ring appeared in 1500-2000 cm\(^{-1}\) region which is also observed in polystyrene spectra. Benzene rings of both monomers show ring stretching bands at 1600 and at 1500 cm\(^{-1}\), and a band at 750 cm\(^{-1}\) associated with C-H out of plane deformation. These bands were found also in copolymers of 2-phenyl-1, 1-dicyanoethylene with vinyl acetate [6], styrene [8] and N-vinyl-2-pyrrolidone [9].

An example of \(^1\)H-NMR analysis of the ST-TSE copolymers is presented in Figure 5.
Figure 4. $^1$H-NMR Spectra of ST-TSE Copolymer (R = 4-butyl) in CDCl$_3$

The broadening of the NMR signals in the spectra of the copolymers is associated with both head-to-head and head-to-tail structures, which formed through the attack of a ST-ended radical on both sides of the TSE monomer unit [10]. The $^1$H-NMR spectra of the ST-TSE copolymers show a broad peak in a 6.0-8.0 ppm region corresponding to phenyl ring protons. The resonance at 2.0 to 2.2 ppm is assigned to ST backbone protons. The peak in 2.5-2.8 ppm is assigned to the one of the chain protons of the TSE monomer unit [10]. Alkyl protons overlapped with chain protons and thus the peak appeared in 0.9-2.0 ppm.
The ST-TSE copolymers were analyzed also by $^{13}$C-NMR spectroscopy. An example of the spectra is presented in Figure 6.
Figure 6. $^{13}$C-NMR Spectrum of ST-TSE Copolymer in CDCl$_3$ (R = 4-isobutyl)

The $^{13}$C-NMR spectra of the copolymers also support the suggested skeletal structure of the copolymers. Thus, in the typical spectrum of the ST-TSE copolymer the assignments of peaks are as follows: 120-150 ppm (phenyl carbons of TSE and ST), 116 ppm (CN), 20-50 ppm (backbone carbons of TSE and ST, and alkyl carbons of TSE ring substitute).

Both IR and NMR data (Figures 4, 5, 7) showed that these are true copolymers, composed of both TSE and ST monomer units.
3.4.2 Properties

The copolymers prepared in the present work are all soluble in dichloromethane, THF, DMF, and chloroform and insoluble in water and methanol. The molecular weight data (Table 2, Figure 8) were collected using gel permeation chromatography (GPC). Polystyrene standards were used. The average molecular weight of the copolymers ranged in 10.8 to 16.4 kDa, typical of styrene copolymers with TSE monomers [4]. A typical GPC trace is presented in Figure 8. Width of the GPC signal gives information about the molecular weight distribution for the copolymers which is similar to the $M_w/M_n$ values. The value of $M_w/M_n$ of all the copolymers is listed in the table 2.

Table 2. Molecular weight and thermal properties of ST-TSE copolymers

<table>
<thead>
<tr>
<th>$R$</th>
<th>$M_w$, kDa</th>
<th>$M_w/M_n$</th>
<th>$T_g$, °C</th>
<th>TGA</th>
<th>Onset of decomp., °C</th>
<th>10 % wt. loss, °C</th>
<th>50 % wt. loss, °C</th>
<th>Residue at 500 °C, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-ethyl</td>
<td>10.8</td>
<td>2.0</td>
<td>86</td>
<td>TGA</td>
<td>139</td>
<td>308</td>
<td>340</td>
<td>5</td>
</tr>
<tr>
<td>4-isopropyl</td>
<td>11.1</td>
<td>2.2</td>
<td>141</td>
<td></td>
<td>63</td>
<td>300</td>
<td>343</td>
<td>7</td>
</tr>
<tr>
<td>4-butyl</td>
<td>11.6</td>
<td>2.7</td>
<td>103</td>
<td></td>
<td>141</td>
<td>336</td>
<td>374</td>
<td>11</td>
</tr>
<tr>
<td>4-isobutyl</td>
<td>15.5</td>
<td>2.4</td>
<td>103</td>
<td></td>
<td>236</td>
<td>311</td>
<td>348</td>
<td>5</td>
</tr>
<tr>
<td>4-t-butyl</td>
<td>16.4</td>
<td>2.2</td>
<td>81</td>
<td></td>
<td>142</td>
<td>314</td>
<td>350</td>
<td>1</td>
</tr>
<tr>
<td>2-ethoxy</td>
<td>10.9</td>
<td>1.6</td>
<td>104</td>
<td></td>
<td>72</td>
<td>309</td>
<td>349</td>
<td>8</td>
</tr>
<tr>
<td>4-hexyloxy</td>
<td>15.7</td>
<td>2.3</td>
<td>113</td>
<td></td>
<td>75</td>
<td>319</td>
<td>352</td>
<td>6</td>
</tr>
<tr>
<td>2-cyano</td>
<td>12.1</td>
<td>1.6</td>
<td>103</td>
<td></td>
<td>207</td>
<td>330</td>
<td>385</td>
<td>0</td>
</tr>
</tbody>
</table>

$T_g$ (transition temperature) was observed by DSC
3.4.3 Thermal Behavior

Thermal behavior of the ST-TSE copolymers was studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Table 2).

DSC analysis shows the glass transition temperature ($T_g$) of polymers. $T_g$ is the temperature of transition from a glassy to a rubbery state [1]. In other words, polymers are glassy below $T_g$ and are rubbery above $T_g$. Figure 9 below shows a typical DSC analysis of ST-TSE copolymer (R = 2-cyano). Here a glass transition temperature is seen at 99.01 °C. The DSC spectra for all ST-TSE copolymers showed only a glass transition temperature. No DSC endotherms (melting temperatures) were seen. Melting temperatures are seen only for crystalline compounds. Hence all the ST-TSE copolymers synthesized are amorphous. The $T_g$ of ST-TSE polymers ranged from 81 to 141 °C (Table 2). All the copolymers had a relatively high $T_g$ in comparison with that of polystyrene ($T_g$ =81-91 °C). Glass transition temperature of copolymer increased due to the presence of TSE structural units which are highly dipolar groups. The highly dipolar TSE structural units led to a decrease in chain mobility. Lower the chain mobility of a compound more is the heat needed for changing the compound from a glassy state to a rubbery state.
Figure 8.

DSC Trace of ST-TSE Copolymer ($R = 2$-cyano)
Information on thermal stability (degradation) of the copolymers was obtained from thermogravimetric analysis and is shown in Figure 10. The decomposition of the copolymers occurred in two steps; a rapid decomposition in the 200-400 °C range followed by a slower decomposition of the formed residue in the 400-800 °C range. The onset of decomposition was in the 200-236 °C range, 10% of weight loss occurred in the 300-336 °C range, and 50% of weight loss occurred in the 340-385°C range. At 500°C, after the first decomposition step, 0-11% of the residue remained (Table 2). The decomposition products were not analyzed in this study, and the mechanism of decomposition has yet to be investigated. No additional experiments were conducted due to focus of this research on the feasibility studies. This type of correlation could be an objective of a separate study.

3.5 Further Discussion

Comparison of the copolymers did not show any significant correlation between the substituent (the number of carbons, the position or the length) and their properties ($T_g$, onset temperature of decomposition, percent of residues, average molecular weight, and relative reactivity/composition). Lack of correlation could be associated with unequal composition and molecular weight of the
copolymers under investigation. Therefore it is hard to separate nature of substitution and free volume ($T_g$) which is also depends on the TSE content and MW of the copolymer. This subject also could be a separate study.

DSC analysis showed that the copolymers are amorphous and thus there is no crystallinity or cross-linking (as they soluble). We did not optimize any application of these copolymers and therefore did not try any processing procedures including use of additives.

4 CONCLUSIONS

Results of these feasibility studies show that the novel copolymers of styrene and trisubstituted ethylene monomers, ring-substituted 2-phenyl-1,1-dicyanoethylenes, RC$_6$H$_4$CH=C(CN)$_2$ (where R is 2-ethyl, 4-isopropyl, 4-butyl, 4-tert-butyl, 4-isobutyl, 2-ethoxy, 4-hexyloxy, and 2-cyano) can be prepared by radical copolymerization at 70ºC.

The monomers were synthesized by Knoevenagel condensation of ring-substituted benzaldehydes with malononitrile, catalyzed by piperidine. 2-Ethyl-substituted monomer was prepared and characterized first time and is not reported in literature.

The structures of resulting copolymers were analyzed by IR, $^1$H- and $^{13}$C-NMR spectroscopy. The average molecular weights of the copolymers were determined by gel permeation chromatography. The copolymer compositions were calculated from nitrogen analysis. Structural and compositional analyses show that the resulting polymers are true copolymers.

The order of the relative reactivity, ratio of rate constants of cross propagation to that of styrene self-propagation ($1/r_1$) was estimated as follows, $4$-tert-butyl (1.45) > 4-isopropyl (1.38) > 2-ethyl (1.37) > 4-hexyloxy (1.33) > 2-cyano (1.32) > 4-butyl (1.04) > 4-isobutyl (1.02) > 2-ethoxy (0.63).

All copolymers have a higher glass transition temperature ($T_g$) than that of polystyrene, as determined by DSC, indicating a substantial decrease in chain mobility of the copolymers due to the high dipolar character of the trisubstituted monomer unit.
Thermal stability studies of the copolymers by thermogravimetric analysis indicated that the copolymers decomposed rapidly in one stage in 200-400 °C range followed by a slower decomposition of the residue at 400-800 °C.

The results of these feasibility studies point to interesting future in-depth research related to correlations of nature of ring-substitution and (1) kinetics of propagation reactions and reliable kinetic models predicting copolymer composition with changes of monomer feed composition; (2) glass transition temperature (mobility of polymer chains); (3) thermal stability.

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