Synthesis and Analysis of Novel Copolymers of Methyl 2--Cyano--3--Phenyl--2--Propenoates with Styrene

Sonia Elena Chavez

DePaul University, sonia_elena@sbcglobal.net

Recommended Citation
Chavez, Sonia Elena, "Synthesis and Analysis of Novel Copolymers of Methyl 2--Cyano--3--Phenyl--2--Propenoates with Styrene" (2014). College of Science and Health Theses and Dissertations. 77.
https://via.library.depaul.edu/csh_etd/77
Synthesis and Analysis of Novel Copolymers of Methyl 2-Cyano-3-Phenyl-2-Propenoates with Styrene

A Thesis
Presented in
Partial Fulfillment of the
Requirements for the Degree of
Master of Science
April 4, 2014

By:
Sonia Elena Chavez

Department of Chemistry
College of Science and Health
DePaul University
Chicago, Illinois
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>3</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>3</td>
</tr>
<tr>
<td>2. Materials and Methods</td>
<td>5</td>
</tr>
<tr>
<td>2.1 Materials</td>
<td>5</td>
</tr>
<tr>
<td>2.2 Analysis Procedures</td>
<td>5</td>
</tr>
<tr>
<td>3. Results and Discussion</td>
<td>7</td>
</tr>
<tr>
<td>3.1 Synthesis of monomers</td>
<td>7</td>
</tr>
<tr>
<td>3.1.1 Methyl 2-cyano-3-(2-acetylphenyl)-2-propenoate</td>
<td>9</td>
</tr>
<tr>
<td>3.1.2 Methyl 2-cyano-3-(3-acetylphenyl)-2-propenoate</td>
<td>9</td>
</tr>
<tr>
<td>3.1.3 Methyl 2-cyano-3-(2-cyanophenyl)-2-propenoate</td>
<td>9</td>
</tr>
<tr>
<td>3.1.4 Methyl 2-cyano-3-[4-(dimethylamino)phenyl]-2-propenoate</td>
<td>10</td>
</tr>
<tr>
<td>3.1.5 Methyl 2-cyano-3-[4-(diethylamino)phenyl]-2-propenoate</td>
<td>10</td>
</tr>
<tr>
<td>3.1.6 Methyl 2-cyano-3-(2-iodophenyl)-2-propenoate</td>
<td>10</td>
</tr>
<tr>
<td>3.1.7 Methyl 2-cyano-3-(4-iodophenyl)-2-propenoate</td>
<td>11</td>
</tr>
<tr>
<td>3.1.8 Methyl 2-cyano-3-[(3-iodo-4-methoxy)phenyl]-2-propenoate</td>
<td>11</td>
</tr>
<tr>
<td>3.1.9 Methyl 2-cyano-3-[(5-iodo-2-methoxy)phenyl]-2-propenoate</td>
<td>11</td>
</tr>
<tr>
<td>3.1.10 Methyl 2-cyano-3-(2,5-dibromophenyl)-2-propenoate</td>
<td>12</td>
</tr>
<tr>
<td>3.1.11 Methyl 2-cyano-3-(3,5-dibromophenyl)-2-propenoate</td>
<td>12</td>
</tr>
<tr>
<td>3.2 Homopolymerization</td>
<td>12</td>
</tr>
<tr>
<td>3.3 Copolymerization</td>
<td>13</td>
</tr>
<tr>
<td>3.3.1 Results of Copolymerization</td>
<td>15</td>
</tr>
<tr>
<td>3.3.2 Monomer Reactivity</td>
<td>16</td>
</tr>
<tr>
<td>3.4 Structure and Properties</td>
<td>18</td>
</tr>
<tr>
<td>3.4.1 Structure</td>
<td>18</td>
</tr>
<tr>
<td>3.4.2 Properties</td>
<td>25</td>
</tr>
<tr>
<td>3.4.3 Thermal Behavior</td>
<td>27</td>
</tr>
<tr>
<td>4. Conclusions</td>
<td>30</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>31</td>
</tr>
<tr>
<td>References</td>
<td>32</td>
</tr>
<tr>
<td>Appendices</td>
<td>34</td>
</tr>
</tbody>
</table>
Abstract

Electrophilic trisubstituted ethylenes, ring-substituted methyl 2-cyano-3-phenyl-2-propenoates, RPhCH=C(CN)CO₂CH₃ (where R is 2-CH₃CO, 3-CH₃CO, 2-CN, 4-Н(CH₃)₂, 4-N(C₂H₅)₂, 2-I, 4-I, 3-I-4-OCH₃, 5-I-2-OCH₃, 2,5-Br₂, 3,5-Br₂), were prepared and copolymerized with styrene. The monomers were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and methyl cyanoacetate, and characterized by CHN elemental analysis, IR, ¹H- and ¹³C-NMR. All the ethylenes were copolymerized with styrene (M₁) in solution at 70 °C, using 1,1-azobis(cyclohexanecarbonitrile) as a radical initiator. Copolymer compositions were calculated from nitrogen elemental analysis and the structures were analyzed by IR, ¹H- and ¹³C-NMR. The order of relative reactivity (1/r₁) for the monomers is 4-I (10.6) > 2-I (6.8) > 2-CN (4.8) > 3-I-4-OCH₃ (2.5) > 3-CH₃CO (2.3) > 5-I-2-OCH₃ (1.5) > 2-CH₃CO (0.8) > 3,5-Br₂ (0.6) > 2,5-Br₂ (0.5) > 4-N(C₂H₅)₂ (0.4) > 4-N(CH₃)₂ (0.3). Relatively high copolymer glass transition temperatures (Tg) in comparison with that of polystyrene indicates decreased chain mobility of the former due to the high dipolar character of the trisubstituted ethylene monomer unit.

1. Introduction

Ring–functionalized trisubstituted ethylenes (TSE, RPhCH=C(CN)CO₂CH₃) continue to attract attention as compounds with interesting properties and as comonomers for the modification of commercial polymers. There are several reports on the potential applications of methyl 2-cyano-3-phenyl-2-propenoates (MCPPs) [1-4]. Dimethylamino ring-substituted MCPPs, amongst other cyanovinylnheteroaromatics, were studied in relation to organic
nonlinear optics [1]. It also was used with benzacetonitriles in a Knoevenagel condensation to produce a novel methodology for the synthesis of α-cyano chalcones [2]. Also diethylamino ring-substituted MCPPs were used for synthesis and study of nonlinear-optical properties of poly-norbornenes [3]. In addition, 3,5-Dibromo ring-substituted MCPP was employed in the synthesis of new phenylsuccinimide derivatives with anticonvulsant properties [4].

It was shown that electrophilic tri- and tetra-substituted olefins are particularly useful in delineating the transition from radical chemistry to ionic chemistry [5]. Previous studies showed that TSE bearing substituents larger than fluorine have very low reactivity in radical homopolymerization due to polar and steric reasons. Although steric interactions preclude homopolymerization of most TSE monomers, their copolymerization with a monosubstituted alkene makes it possible to overcome these steric problems [6]. 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 [7-9] show a tendency toward the formation of alternating copolymers. Unsubstituted phenyl methyl 2-cyano-3-phenyl-2-propenoate was copolymerized with styrene [10], vinyl acetate [11], ethyl, n-butyl, i-butyl, t-butyl, 2-chloroethyl, and phenyl vinyl ethers [12].

With the objective of designing novel structures that could serve as a spring board for further development of novel materials with new properties and applications, and in continuation of our studies of the monomer structure-reactivity correlation in the radical copolymerization of TSE monomers [13-15] we have prepared some ring-substituted methyl 2-cyano-3-phenyl-2-propenoates, RPhCH=C(CN)CO₂CH₃, where R is 2-CH₃CO, 3-CH₃CO, 2-CN, 4-N(CH₃)₂, 4-N(C₂H₅)₂, 2-I, 4-I, 3-I-4-OCH₃, 5-I-2-OCH₃, 2,5-Br₂, 3,5-Br₂. We have also explored the feasibility of their copolymerization with styrene. To the best of our knowledge,
there have been no reports on styrene copolymerization with these ring-substituted MCPP monomers.

2. MATERIALS AND METHODS

2.1 Materials

The synthesis of the TSE monomer was carried out using 2-acetyl, 3-acetyl, 2-cyano, 4-(dimethylamino), 4-diethylamino, 2-iodo, 4-iodo, 3-iodo-4-methoxy, 5-iodo-2-methoxy, 2,5-dibromo, or 3,5-dibromo-benzaldehyde, methyl cyanoacetate, and piperidine. To recrystallize the TSE product, 2-isopropanol was used. Copolymerization was performed using styrene (ST), 1,1-azobis(cyclohexanecarbonitrile) (ABCN), toluene, and methanol. Analysis of TSE monomers and copolymers were performed using chloroform-d (99.8 atom % D) and dichloromethane as solvents, but tetrahydrofuran (THF) was only used for the GPC analysis of the copolymers as a solvent. The materials were purchased and used as received from Sigma-Aldrich.

2.2 Analysis Procedures

A differential scanning calorimeter (TA instruments DSC Q10) was used to measure the melting points of the TSE monomer and glass transition temperature \( T_g \) of the copolymers. The range of the thermal scans for the DSC was 20-250 °C with a heating rate of 15 °C/min. In addition, the sample was encased in an aluminum pan. From the DSC heating curve the \( T_g \) was determined by taking the midpoint of a straight line between the onset and endpoint peaks.

Thermogravimetric analysis (TA instruments TGA Q50) was used to measure the thermal stability of the copolymer. The sample was loaded on a platinum pan and placed
into the instrument’s oven. The range of the thermal scans for the TGA was from room
temperature to 800 °C with a heating rate of 20 °C/min.

To determine the functional groups of the TSE monomer and copolymer, infrared
spectra an ABB FT-IR FTLA 2000 was used with potassium bromide (KBr) plates. The
sample for the IR was made by adding a small amount of monomer or polymer into a
scintillation vial with enough dichloromethane to dissolve the sample.

Gel permeation chromatography (GPC) is considered a type of size exclusion
chromatography. It can be used to determine molecular weight averages and
polydispersity index. The GPC instrument is made up of a HPLC Pump Model 426 by Altech
at an elution rate of 1.0 ml/min, a PolyAnalytik PAS-104-M-L column at 25 °C, Viscotek TDA
(Triple Detector Array) 302 and Viscotek Model 2501 UV detector. It was used to
determine the molecular weights of the copolymers relative to polystyrene standard in
THF solutions (sample concentrations 0.8% w/v). The GPC sample was prepared by adding
20.0 mg of the polymer and 2.22 g of THF to a scintillation vial. Once dissolved the sample
is filtered before injecting the sample into the instrument. Spectra of $^1$H- and $^{13}$C-NMR
spectra were obtained from a Bruker Avance 300 MHz spectrometer with a 10-25% (w/v)
solution of monomer or copolymer in CDCl$_3$.

The Quantitative Technologies Inc. (New Jersey) performed the elemental analyses
for the monomer and copolymer. From the results, the CHN wt% the monomers purity was
confirmed and N wt% of polymer was used to determine the monomer composition.

3. RESULTS AND DISCUSSION

3.1 Synthesis of Monomers
Synthesis of the TSE monomers utilizes the piperidine catalyzed Knoevenagel condensation [14] reaction of a ring-substituted benzaldehyde with methyl cyanoacetate (Figure 1). The mechanism of the reaction can be seen in Figure 2 [15,16].

\[
\text{Figure 1. TSE Monomer Synthesis (R= 2-Acetyl, 3-acetyl, 2-cyano, 4-(dimethylamino), 4-diethylamino, 2-iodo, 4-iodo, 3-iodo-4-methoxy, 5-iodo-2-methoxy, 2,5-dibromo, or 3,5-dibromo benzaldehyde)}
\]
Figure 2. The mechanism for the TSE monomer synthesis

For all TSE monomers the same preparation procedure was completed, using equimolar amounts of the appropriate ring-substituted benzaldehyde and methyl cyanoacetate. The benzaldehyde and cyanoacetate were added to a scintillation vial, followed by a 2-3 drops of piperidine. If necessary, the mixture was heated in a 40 °C water bath to melt the aldehyde and methyl cyanoacetate. The reaction mixture was then allowed to stir at room temperature. To isolate the crystalline monomers, a filtration was performed to purify the monomer followed by a recrystallization done using isopropanol.
The purified product was placed in a room temperature vacuum oven to dry and then analyzed by DSC, TGA, IR, $^1$H- and $^{13}$C-NMR spectroscopy (recorded in deuterated chloroform), and CHN elemental analysis. The characterization results for the TSE monomers are as follow:

### 3.1.1 Methyl 2-cyano-3-(2-acetylphenyl)-2-propenoate

Yield 54%; mp 107 °C; $^1$H-NMR δ 8.81 (s, 1H, CH=), 8.03, 7.84, 7.61 (m, 4H, Ph), 4.00 (s, 3H, OCH₃), 2.71 (s, 3H, CH₃CO); $^{13}$C-NMR δ 200.1 (CH₃C=O), 1162.5 (C=O), 158.9 (HC=), 137.2, 133.2, 132.8, 130.5, 130.0 (Ph), 114.4 (CN), 104.8 (C=), 53.6 (OCH₃), 27.7 (COCH₃); IR (cm⁻¹): 2989 (m, C-H), 2228 (m, CN), 1730 (s, C=O), 1207 (s, C-O-CH₃), 768, 710 (s, C-H out of plane). Anal. Calcd. for C₁₃H₁₁NO₃: C, 68.11; H, 4.84; N, 6.11; Found: C, 66.33; H, 4.65; N, 6.33.

### 3.1.2 Methyl 2-cyano-3-(3-acetylphenyl)-2-propenoate

Yield 45%; mp 128 °C; $^1$H-NMR δ 8.64 (s, 1H, CH=), 7.92 - 7.63 (m, 4H, Ph), 3.98 (s, 3H, OCH₃), 2.21 (s, 3H, CH₃CO); $^{13}$C-NMR δ 195.8 (CH₃C=O), 163.7 (C=O), 153.2 (HC=), 137.8, 134.6, 132.4, 131.6, 131.3, 129.8 (Ph), 115.2 (CN), 104.1 (C=), 53.6 (OCH₃), 27.5 (COCH₃); IR (cm⁻¹) 3063, 3038 (m, C-H), 2220 (m, CN), 1738(C=O), 1275, 1252 (s, C-O-CH₃), 795, 677 (s, C-H out of plane). Anal. Calcd. for C₁₃H₁₁NO₃: C, 68.11; H, 4.84; N, 6.11; Found: C, 67.69; H, 4.65; N, 5.72.

### 3.1.3 Methyl 2-cyano-3-(2-cyanophenyl)-2-propenoate

Yield 54%; mp 141 °C; $^1$H-NMR δ 8.62 (s, 1H, CH=), 8.42-7.66 (m, 4H, Ph), 3.19 (s, 3H, CH₃); $^{13}$C-NMR δ 149.8 (=CH), 134.1, 133.7, 132.5, 129.1 (Ph), 116.4 (CN); IR (cm⁻¹) 2961 (m, C-H), 2226, 2206 (m, CN), 1749 (C=O), 1281 (s, C-O-CH₃), 768 (s, C-H out of plane). Anal. Calcd. for C₁₂H₈N₂O₂: C, 67.92; H, 3.80; N, 13.20. Found: C, 67.69; H, 3.90; N, 12.80.
3.1.4 Methyl 2-cyano-3-[4-(dimethylamino)phenyl]-2-propenoate

Yield 28%; mp 131 °C; \(^1\)H-NMR \(\delta 8.12\) (s, 1H, CH=), 7.70, 6.67 (d, 4H, Ph), 3.90 (d, 6H, N(CH\(_3\))\(_2\), 3.84 (s, 3H, OCH\(_3\)); \(^{13}\)C-NMR \(\delta 163.4\) (C=O), 155.1 (=CH), 153.5, 136.2, 128.5, 128.1, 124.7, (Ph), 116.3 (CN), (C=), 52.4 (OCH\(_3\)); IR (cm\(^{-1}\)) 2919 (m, C-H), 2214 (m, CN), 1661 (C=O), 1232 (s, C-O-CH\(_3\)) 825, 814 (s, C-H out of plane). Anal. Calcd. for C\(_{13}\)H\(_{14}\)N\(_2\)O\(_2\): C, 67.81; H, 6.13; N, 12.17. Found: C, 66.79; H, 5.98; N, 12.07.

3.1.5 Methyl 2-cyano-3-[4-(diethylamino)phenyl]-2-propenoate

Yield 90%; mp 97 °C; \(^1\)H-NMR \(\delta 8.16\) (s, 1H, CH=), 7.70, 6.71 (d, 4H, Ph), 3.52 (q, 4H, NCH\(_2\)), 1.34 (m, 9H, CH\(_3\)); \(^{13}\)C-NMR \(\delta 165.0\) (C=O), 154.6 (=CH), 151.7, 134.6, 119.0, 111.2 (Ph), 117.8 (CN), 93.2 (C=), 53.7 (OCH\(_3\)), 44.1 (CH\(_2\)), 12.4 (CH\(_3\)); IR (cm\(^{-1}\)) 2932 (m, C-H), 2214 (m, CN), 1739 (C=O), 1277, 1300 (s, C-O-CH\(_3\)) 820, 710 (s, C-H out of plane). Anal. Calcd. for C\(_{15}\)H\(_{18}\)N\(_2\)O\(_2\): C, 69.74; H, 7.02; N, 10.84. Found: C, 69.75; H, 7.17; N, 10.63.

3.1.6 Methyl 2-cyano-3-(2-iodophenyl)-2-propenoate

Yield 43%; mp 97 °C; \(^1\)H-NMR \(\delta 8.5\) (s, 1H, CH=), 8.2, 8.1, 7.5, 7.2 (m, 4H, Ph), 4.0 (s, 3H, CH\(_3\)); \(^{13}\)C-NMR \(\delta 163.1\) (C=O), 158.8 (HC=), 140.0, 135.2, 133.5, 130.0, 128.9 (Ph), 114.6 (CN), 101.4 (C=), 53.2 (CH\(_3\)); IR (cm\(^{-1}\)) 2955 (m, C-H), 2228 (m, CN), 1732 (s, C=O), 1283, 1261 (s, C-O-CH\(_3\)), 704 (s, C-H out of plane). Anal. Calcd. for C\(_{11}\)H\(_8\)INO: C, 42.20; H, 2.58; N, 4.47. Found: C, 42.34; H, 2.34; N, 4.82.
3.1.7 *Methyl 2-cyano-3-(4-iodophenyl)-2-propenoate.*

Yield 66%; mp 114 °C; $^1$H-NMR $\delta$ 8.19 (s, 1H, CH=), 7.90, 7.72 (q, 4H, Ph), 4.01 (s, 3H, CH$_3$); $^{13}$C-NMR $\delta$ 163.1 (C=O), 153.0 (HC=), 138.9, 132.0 (Ph), 53.2 (CH$_3$); IR (cm$^{-1}$) 3034, 2987 (m, C-H), 2222 (m, CN), 1724 (s, C=O), 1277, 1209 (s, C-O-CH$_3$), 820, 760 (s, C-H out of plane). Anal. Calcd. for C$_{11}$H$_8$INO: C, 42.20; H, 2.58; N, 4.47. Found: C, 44.12; H, 2.41; N, 4.32.

3.1.8 *Methyl 2-cyano-3-[(3-iodo-4-methoxy)phenyl]-2-propenoate*

Yield 90%; mp 160 °C; $^1$H-NMR $\delta$ 8.31 (s, 1H, CH=), 8.24–6.92 (m, 3H, Ph), 3.90 (s, 3H, PhOCH$_3$), 3.81 (s, 3H, OCH$_3$); $^{13}$C-NMR $\delta$ 153.1 (HC=), 143.2, 133.5, 115.0, (Ph), 57.4 (PhOCH$_3$), 53.8 (CH$_3$); IR (cm$^{-1}$) 3013, 2987 (m, C-H), 2220 (m, CN), 1726 (s, C=O), 1280, 1202 (s, C-O-CH$_3$), 812, 762 (s, C-H out of plane). Anal. Calcd. for C$_{12}$H$_{10}$NO$_3$: C, 42.01; H, 2.94; N, 4.08. Found: C, 41.83; H, 2.89; N, 3.97.

3.1.9 *Methyl 2-cyano-3-[(5-iodo-2-methoxy)phenyl]-2-propenoate.*

Yield 80%; mp 167 °C; $^1$H-NMR $\delta$ 8.61 (s, 1H, CH=), 8.61, 7.82, 6.74 (m, 3H, Ph), 3.95 (s, 3H, PhOCH$_3$), 3.90 (s, 3H, CH$_3$); $^{13}$C-NMR $\delta$ 163.2 (C=O), 158.9 (HC=), 148.2, 143.4, 137.2, 124.1, 115.6, 84.6 (Ph), 103.7 (C=), 57.2 (PhOCH$_3$), 53.6 (CH$_3$); IR (cm$^{-1}$) 2980 (m, C-H), 2225 (m, CN), 1746 (s, C=O), 1650 (m, C=C), 764 (s, C-H out of plane). Anal. Calcd. for C$_{12}$H$_{10}$NO$_3$: C, 42.01; H, 2.94; N, 4.08. Found: C, 41.88; H, 2.58; N, 3.99.
3.1.10 **Methyl 2-cyano-3-(2,5-dibromophenyl)-2-propenoate.**

Yield 52%; mp 138 °C; \(^1\)H-NMR \(\delta 8.14\) (s, 1H, CH=), 7.51, 7.27 (m, 3H, Ph), 3.99 (s, 3H, OCH₃); \(^{13}\)C-NMR \(\delta 163.8\) (C=O), 153.4 (HC=), 136.4, 134.9, 133.1, 132.5, 125.0, 122.1 (Ph), 114.2 (CN), 107.2 (C=), 54.3 (OCH₃); IR (cm\(^{-1}\)) 3078, 2920, 2837 (m, C-H), 2228 (m, CN), 1680 (s, C=O), 1614 (m, C=C), 1260, 1180 (s, C-O-CH₃), 887, 825 (s, C-H out of plane). Anal. Calcd. for C\(_{11}\)H\(_7\)NO\(_2\): C, 38.30; H, 2.05; N, 4.06. Found: C, 38.02; H, 1.95; N, 3.98.

3.1.11 **Methyl 2-cyano-3-(3,5-dibromophenyl)-2-propenoate.**

Yield 92%; mp 159 °C; \(^1\)H-NMR \(\delta 8.12\) (s, 1H, CH=), 7.92 (m, 3H, Ph), 3.99 (s, 3H, OCH₃); \(^{13}\)C-NMR \(\delta 162.6\) (C=O), 152.0 (HC=), 138.1, 134.5, 132.9, 123.7 (Ph), 114.5 (CN), 105.2 (C=), 54.3 (OCH₃); IR (cm\(^{-1}\)) 3082, 2927, 2837 (m, C-H), 2226 (m, CN), 1698 (s, C=O), 1550 (m, C=C), 1263, 1209 (s, C-O-CH₃), 875, 750 (s, C-H out of plane). Anal. Calcd. for C\(_{11}\)H\(_7\)NO\(_2\): C, 38.30; H, 2.05; N, 4.06. Found: C, 38.08; H, 1.65; N, 4.01.

3.2 **Homopolymerization**

An attempted homopolymerization of the TSE monomers in the presence of ABCN 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 [10]. Homopolymerization of ST under conditions identical to those in copolymerization experiments yielded 18.3% of polystyrene, when polymerized for 30 min.
3.3 Copolymerization

Copolymerization of the TSE and Styrene was conducted under radical conditions, employing ABCN as a radical initiator (Figure 3). The mechanism for the copolymerization can be seen in Figure 4.

**Figure 3.** ST-TSE Copolymerization Reaction (2-Acetyl, 3-acetyl, 2-cyano, 4-(dimethylamino), 4-diethylamino, 2-iodo, 4-iodo, 3-iodo-4-methoxy, 5-iodo-2-methoxy, 2,5-dibromo, or 3,5-dibromo benzaldehyde)
Figure 4. The mechanism for the copolymerization
Styrene, 1,1-azobis(cyclohexanecarbonitrile) (ABCN), and toluene were used as received. Copolymers of styrene and the TSE monomers were prepared in 25-mL glass screw cap vials with ST/MCPP=2/1 (mol), the monomer feed using 0.12 mol/L of ABCN at an overall monomer concentration 2.44 mol/L in 10 mL of toluene. The copolymerization was conducted at 70 °C. After five hours, the mixture was cooled to room temperature, and precipitated dropwise in methanol. The copolymers were isolated by vacuum filtration and dried in a vacuum oven.

3.3.1 Results of Copolymerization

The copolymerization of styrene with ring-substituted methyl 2-cyano-3-phenyl-2-propenoates resulted in formation of copolymers (Table 1). Weight-average molecular masses of the copolymers ranged from 8.1 to 31.4 kD.

**Table 1:** Copolymerization of styrene (m<sub>1</sub>) with ring-substituted methyl 2-cyano-3-phenyl-2-propenoates RPhCH=C(CN)CO<sub>2</sub>CH<sub>3</sub> (m<sub>2</sub>)

<table>
<thead>
<tr>
<th>R</th>
<th>Yield&lt;sup&gt;a&lt;/sup&gt;, wt%</th>
<th>N, wt%</th>
<th>m&lt;sub&gt;2&lt;/sub&gt; in pol., mol%</th>
<th>r&lt;sub&gt;1&lt;/sub&gt; (m&lt;sub&gt;1&lt;/sub&gt;/m&lt;sub&gt;2&lt;/sub&gt;)&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>1/r&lt;sub&gt;1&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-acetyl</td>
<td>13.8</td>
<td>2.58</td>
<td>24.9</td>
<td>1.2</td>
<td>0.8</td>
</tr>
<tr>
<td>3-acetyl</td>
<td>17.3</td>
<td>3.15</td>
<td>32.6</td>
<td>0.4</td>
<td>2.3</td>
</tr>
<tr>
<td>2-cyano</td>
<td>14.1</td>
<td>7.14</td>
<td>36.6</td>
<td>0.2</td>
<td>4.8</td>
</tr>
<tr>
<td>4-(dimethylamino)</td>
<td>12.7</td>
<td>3.45</td>
<td>15.2</td>
<td>3.5</td>
<td>0.3</td>
</tr>
<tr>
<td>4-diethylamino</td>
<td>14.5</td>
<td>3.62</td>
<td>16.8</td>
<td>2.8</td>
<td>0.4</td>
</tr>
<tr>
<td>2-iodo</td>
<td>10.3</td>
<td>2.69</td>
<td>45.8</td>
<td>0.1</td>
<td>6.8</td>
</tr>
<tr>
<td>4-iodo</td>
<td>13.2</td>
<td>2.73</td>
<td>34.2</td>
<td>0.1</td>
<td>10.6</td>
</tr>
<tr>
<td>3-iodo-4-methoxy</td>
<td>18.3</td>
<td>2.35</td>
<td>29.2</td>
<td>0.4</td>
<td>2.5</td>
</tr>
<tr>
<td>5-iodo-2-methoxy</td>
<td>12.3</td>
<td>2.21</td>
<td>26.4</td>
<td>0.7</td>
<td>1.5</td>
</tr>
<tr>
<td>2,5-dibromo</td>
<td>8.6</td>
<td>1.76</td>
<td>18.8</td>
<td>1.9</td>
<td>0.5</td>
</tr>
<tr>
<td>3,5-dibromo</td>
<td>11.3</td>
<td>1.86</td>
<td>20.3</td>
<td>1.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

<sup>a</sup>Polymerization time was 5 hours

Yields for the copolymers were kept at a low percentage to account for the monomers different reactivity. The difference in reactivity can cause copolymer
composition to drift, which is why yields are kept low. By keeping the monomer feed about equimolar the change in compositional ratio of the monomer feed, which occurs when the reaction proceeds, could be avoided. The composition of the copolymers was determined based on the nitrogen content (table 1).

3.3.2 Monomer Reactivity

Copolymerization of two different monomers can produce two reactive centers with radical chain ends. In this case, the M₁ and M₂ monomers are ~~~ST• and ~~~TSE•. From these reactive centers, four propagation reactions can occur and are shown below:

<table>
<thead>
<tr>
<th>Radical Chain End</th>
<th>Monomer</th>
<th>New Radical Chain End</th>
</tr>
</thead>
<tbody>
<tr>
<td>~~~ST•</td>
<td>ST</td>
<td>~~~ST-ST•</td>
</tr>
<tr>
<td>~~~ST•</td>
<td>TSE</td>
<td>~~~ST-TSE•</td>
</tr>
<tr>
<td>~~~TSE•</td>
<td>TSE</td>
<td>~~~TSE-TSE•</td>
</tr>
<tr>
<td>~~~TSE•</td>
<td>ST</td>
<td>~~~TSE-ST•</td>
</tr>
</tbody>
</table>

where \( k_{11} \) and \( k_{22} \) are rate constants for homopropagation of the TSE and ST respectively, and \( k_{12} \) and \( k_{21} \) are rate constants for cross-propagation between the TSE and ST. In addition, the four reactions are assumed to be irreversible.

To qualitatively calculate the monomer reactivates of the copolymers, the obtained copolymer data was used. The data was obtained with equimolar of the monomer feed. In addition, the copolymer composition equation (Equation 5) is derived from the terminal model of copolymerization and by using the rates of disappearance of the two monomers [6]. From the copolymer composition equation the reactivity of ST with the various monomers used can be estimated.

\[
\frac{m_1}{m_2} = \frac{[M_1] (r_1 [M_1] + [M_2])}{[M_2] ([M_1] + r_2 [M_2])} \quad (5)
\]
In the copolymer composition equation, $m_1$ and $m_2$ represent the mole fraction of the ST and TSE monomers. The concentrations of ST and TSE in the monomer feed are represented as $[M_1]$ and $[M_2]$, with the monomer reactivity ratios of the propagation to cross-propagation are defined by $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. The monomer reactivity ratio represent the ratio of the reactive propagating species rate constant that is being added by its own type of monomer to the rate constant of the other monomer that is being added [6]. But if self-propagation of the TSE monomers does not occur, the equation for the relative reactivity is produced to be:

$$ r_1 = \frac{m_1}{m_2} - 1 \quad (6) $$

This occurs when $k_{22}$ and $r_2$ equal to 0 and the monomer feed is at equimolar ($[m_1]/[m_2]=2$). In addition, the relative reactivity equation of ST radical with the TSE monomers can also be used in the absence of self-propagation.

$$ \frac{1}{r_1} = \frac{1}{\frac{m_1}{m_2} - 1} \quad (7) $$

For equation 7 to hold true, it must be assumed that minimal copolymer composition drift occurs at equimolar monomer feed with the given conversion. To estimate the reactivity of ST being the end radical in the reaction, the information collected in table (1) was used. It was found, that the relative reactivity ($1/r_1$) of the TSE monomers is 4-1 (10.6) > 2-1 (6.8) > 2-CN (4.8) > 3-1-4-OCH$_3$ (2.5) > 3-CH$_3$CO (2.3) > 5-1-2-OCH$_3$ (1.5) > 2-CH$_3$CO (0.8) > 3.5-Br$_2$ (0.6) > 2.5-Br$_2$ (0.5) > 4-N(C$_2$H$_5$)$_2$ (0.4) > 4-N(CH$_3$)$_2$ (0.3). The composition of the copolymers could not be predicted due to the lack of number of samples and information.
3.4 Structure and Properties

The copolymerization between the TSE monomers and ST was confirmed through the comparison of copolymer and styrene spectra. Only one example is presented, because the copolymers have similar results. Additional spectra can be found in the appendices.

3.4.1 Structure

Characterization of the copolymer structure was examined through the use of IR and NMR spectroscopy. The functional groups present in the copolymer were examined through the use of FT-IR (Fourier transform infrared) spectroscopy (Figure 5). To confirm the copolymerization of the TSE monomer and ST, the monomer, copolymer and polystyrene IR spectra were compared.

Figure 3. The IR spectra of TSE monomer (R=4-diethylamino) with the characterizing functional groups with the axis as Transmittance (%) versus wavenumber cm$^{-1}$.
**Figure 4.** The IR spectra of styrene with the characterizing functional groups [20].

**Figure 5.** The IR spectra of ST-TSE copolymer (R=4-diethylamino) with the characterizing functional groups.
From Figure 3 it was found that the TSE monomer contained bands in the following regions: 2932 cm$^{-1}$ (m, C-H), 2214 cm$^{-1}$ (m, CN), 1739 cm$^{-1}$ (C=O), and 1277 cm$^{-1}$, 1300 cm$^{-1}$ (s, C-O-CH$_3$). In addition, in Figure 3 the % transmittance exceeds 100%, which can be caused by difference of the reference sample and measurement target surface [17]. The styrene IR contained a C-H bond between 3100-3000 cm$^{-1}$, a C=C double bond for vinyl and aromatic carbons at 1552 cm$^{-1}$ and 1500 cm$^{-1}$, and 1000 cm$^{-1}$, 950 cm$^{-1}$ (=CH). It was found that the copolymer spectra share overlapping bands in 3346-2600 cm$^{-1}$ region that represents the C-H stretch vibrations. The bands that are represented by the TSE monomer are found in the following regions: 2239-2245 cm$^{-1}$ (w, CN), 1735-1740 cm$^{-1}$ (s, C=O), and 1225-1242 cm$^{-1}$ (m, C-O). Both monomers also show bands at 1493-1495 cm$^{-1}$ and 1450-1560 cm$^{-1}$ corresponding to the ring stretching of the benzene rings. A doublet is also present at 750-770 cm$^{-1}$ and 690-683 cm$^{-1}$ to represent C-H out of plane deformations. From the bands it can be seen that the ST-TSE monomer functional groups are present in the copolymerization.

NMR spectroscopy was used to determine the number of unique carbon and hydrogen atoms present in the molecules. From the $^1$H-NMR spectra it was found that the copolymers contained a broad double peak in a 6.00-8.00 ppm, which represent the phenyl ring protons. The spectra also contained a peak around 4.20-3.90 ppm that corresponds to the methoxy group in the copolymers. In the spectra, the broad resonance at 3.80-2.20 ppm that defined the methine proton corresponded to the TSE monomer and the methylene protons of the ST monomer unit adjacent to the propenoate units. These trends can be seen in Figure 6 of the proton spectrum of the ST-TSE copolymer (R=3-iodo-4-methoxy) with Figure 7 and 8 showing the proton spectrum of the TSE and ST monomers.
Figure 6. $^1$H-NMR Spectra of ST-TSE copolymer (R= 3-iodo-4-methoxy)

Figure 7. $^1$H-NMR Spectra of TSE monomer (R= 3-iodo-4-methoxy)
Figure 8. $^1$H-NMR Spectra of ST monomer [20]

The methylene protons on the TSE monomer unit are subject to more deshielding than the protons found in the polystyrene. In addition, the signals associated with the low and high field components are found to belong to the TSE monomer unit in a head-to-tail and head-to-head structures due to the broadening of the NMR signals [18-19].

The suggested skeletal structure of the copolymer was supported by the $^{13}$C-NMR spectra. The $^{13}$C-NMR spectra contained carbonyl carbon between 168.0 - 163.0 ppm. In addition, quaternary carbons belonging to both phenyls are found in the range of 134.0-158.0. Phenyl carbons are also found in the range of 120.0-145.0 ppm with the carbons bound to the amine being found at 110.0-120.0 ppm. Carbons belonging to methine carbons and methoxy of the TSE copolymer are found between 50.0-60.0 ppm with the ST methine and methylene at 45.0-47.0 ppm and 40.0-43.0 ppm. These trends can be seen in Figure 9 with the monomer
spectra seen in Figure 10 and 11. Both the IR and NMR data show these are true copolymers that are composed of the ST and TSE monomer units.

**Figure 9.** $^{13}$C-NMR spectrum of ST-TSE copolymer (R= 4-diethylamino)
Figure 10. $^{13}$C-NMR spectrum of TSE monomer (R= 4-diethylamino)

Figure 11. $^{13}$C-NMR spectrum of ST monomer [20]
3.4.2 Properties

The prepared ST-TSE copolymers are found to be soluble in CHCl₃, THF, ethyl acetate, and DMF but insoluble in ethyl ether, methanol, and petroleum ether. In addition, the molecular weight of the copolymers is of great importance for solubility. It can help to determine other physical properties, which includes strength, stiffness, and viscosity. To find the molecular weight of these polymers gel permeation chromatography (GPC) was used. GPC is a size exclusion chromatography, which separates analytes on the basis of size. It is also one of the most convenient techniques for characterizing a polymer's molecular weight distribution.

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

<table>
<thead>
<tr>
<th>R</th>
<th>Mw, kD</th>
<th>$T_g$, °C</th>
<th>TGA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Onset of decomp., °C</td>
</tr>
<tr>
<td>2-acetyl</td>
<td>16.6</td>
<td>159</td>
<td>250</td>
</tr>
<tr>
<td>3-acetyl</td>
<td>17.3</td>
<td>141</td>
<td>275</td>
</tr>
<tr>
<td>2-cyano</td>
<td>20.8</td>
<td>165</td>
<td>247</td>
</tr>
<tr>
<td>4-(dimethylamino)</td>
<td>9.5</td>
<td>145</td>
<td>274</td>
</tr>
<tr>
<td>4-diethylamino</td>
<td>8.1</td>
<td>125</td>
<td>200</td>
</tr>
<tr>
<td>2-iodo</td>
<td>15.1</td>
<td>165</td>
<td>260</td>
</tr>
<tr>
<td>4-iodo</td>
<td>28.4</td>
<td>185</td>
<td>256</td>
</tr>
<tr>
<td>3-iodo-4-methoxy</td>
<td>24.0</td>
<td>167</td>
<td>207</td>
</tr>
<tr>
<td>5-iodo-2-methoxy</td>
<td>29.1</td>
<td>160</td>
<td>267</td>
</tr>
<tr>
<td>2,5-dibromo</td>
<td>13.4</td>
<td>173</td>
<td>220</td>
</tr>
<tr>
<td>3,5-dibromo</td>
<td>31.4</td>
<td>179</td>
<td>257</td>
</tr>
</tbody>
</table>

$^aT_g$ transition was observed by DSC
Figure 12. Gel Permeation Chromatogram of the average molecular weight distribution of the ST-TSE copolymer (R= 2-acetyl) with the average molecular weight at 16.6 kD
From Figure 12 the molecular weight was found to be 8 kD for copolymer (R=2-acetyl). The average molecular weight for the ST-TSE copolymer ranged from 8.1 - 31.4 kD.

3.4.3 Thermal Behavior

Since copolymers are expected to withstand different temperatures, their thermal behavior is of great interest. The use of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) was used to study the thermal behavior of the ST-TSE copolymers. DSC is a thermal technique that looks at how the materials heat capacity changes due to temperature. From a DSC trace, several transitions can be determined, which includes melting temperatures, glass transitions, phases changes and curing. In this study the DSC is used to determine the glass transition temperature ($T_g$) of the copolymers. The $T_g$ of the copolymer is the temperature at which the transition of the glassy state to the rubbery state occurs [6].
From Figure 13 the $T_g$ of the copolymer (R=2-acetyl) was found to be 159.48 °C. In table 2 the results of the DSC analysis are presented. Since the $T_g$ of the copolymers are high compared to the polystyrene $T_g$ at 95°C, the copolymer chain mobility decreases due to the increase in dipolar character of the copolymer structure.

Information on the degradation of the copolymers was obtained using the TGA, a trace of which can be seen in Figure 8 for ST-TSE copolymer (R=4-diethylamino).
Figure 14. The TGA trace of ST-TSE copolymer (R=4-diethylamino) showing the decomposition of the copolymer in the green trace

A standard trace of the decomposition of a copolymer can be seen in Figure 14. The copolymer decomposition occurred in two steps. The first step is a rapid decomposition of nitrogen in the range 200-500 °C, with residue around 2.6-21.2 % wt. In addition, the onset occurred at a range of 200-275 °C with the range of 10% of weight loss around 243-347 °C for the copolymers (Table 2). The second step of the trace shows decomposition in the range 500-800 °C. Loss of 50% of weight occurred in 340-395 °C and 2-21% residue still remained at 500 °C (table 2). But analyses on the decomposition of the products were not completed in this study and investigation on the mechanism has yet been completed.
4. Conclusions

Electrophilic trisubstituted ethylenes, ring-substituted methyl 2-cyano-3-phenyl-2-propenoates, were prepared via a base catalyzed condensation of substituted benzaldehydes and methyl cyanoacetate. Diversification of aromatic groups, including electron-withdrawing and electron-donating substituents has led to preparation of novel styrene copolymers. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, $^1$H- and $^{13}$C-NMR. Relatively high glass transition temperatures of the copolymers, in comparison with that of polystyrene, indicate a substantial decrease in chain mobility of the copolymers due to the high dipolar character of the trisubstituted ethylene monomer unit. The thermal gravimetric analysis indicated that the copolymers decompose in two steps, first in the 200-500 °C range with residue (2.6-21.3 %wt), which then decomposed in the 500-800 °C range.
Acknowledgements

I am grateful to acknowledge partial funding from the Coating Industry Education Foundation (CIEF), Chicago Society of Coating Technology, and Office of Sponsored Programs and Research of DePaul University. I was partially supported by a CIEF graduate fellowship. In addition, I would also like to thank my advisor Dr. Kharas and the Chemistry Department faculty and staff.
References

14. Kharas, G.B., Christensen, J.L., Cichanski, D.J., Goldman, K.E., Gordon, C.L., Knowles, L.M.,


105.57 °C. Figure 1. DSC spectra of the TSE monomer (R=2-acety) showing the melting point at

Appendices

Appendix I: Monomer DSC Trace
Figure 1.2. DSC spectra of the TSE monomer (R=3-acetyl) showing the melting point at 128.13 °C.
Figure 1.3. DSC spectra of the TSE monomer (R=2-cyano) showing the melting point at 140.54°C.
Figure 1.4. DSC spectra of the TPE monomer (R= 4-dimethylaminophenyl) showing the melting point at 130.69°C.
Figure I.5. DSC spectra of the TSE monomer (R=4-diethylamin) showing the melting point at 89.14°C.
Figure 1.6. DSC spectra of the TSE monomer (R=2-iodo) showing the melting point at 96.63°C.
Figure 1.7. DSC spectra of the TSE monomer (R = 4-iodo) showing the melting point at 113.98°C.
Figure 18. DSC spectra of the TSE monomer (R=3-iodo-4-methoxy) showing the melting point at 159.5°C.
Figure 1.9. DSC spectra of the TSE monomer (R= 5-iodo-2-methoxy) showing the melting point at 166.89°C.
Figure 10. DSC spectra of the TSE monomer (R=2,5-dibromo) showing the melting point at 137.80°C.
Figure I.11. DSC spectra of the TSE monomer (R=3,5-dibromo) showing the melting point at 159.2°C.
Figure II.1. The IR spectra of ST-TE copolymer (R=2-acetyl) with the characterizing functional groups.
Figure II.2. The IR spectra of ST-1SE copolymer (R=3-acetyl) with the characterizing functional groups.
Figure II.3. The IR spectra of TSE monomer (R=2-cyano) with the characterizing functional groups.
Figure 11.4. The IR spectra of TSE monomer (R=4-dimethylaminophenyl) with the characterizing functional groups

![Image of IR spectra](image_url)
Figure II.5. The IR spectra of TSE monomer (R=2-iodo) with the characterizing functional groups.
Figure II.6. The IR spectra of TSE monomer (R=4-ido) with the characterizing functional groups.
Figure II.7. The IR spectra of TSE monomer (R=3-iodo-4-methoxy) with the characterizing functional groups.
Figure II.8. The IR spectra of TSE monomer (R=5-iodo-2-methoxy) with the characterizing functional groups.
Figure II.9. The IR spectra of TSE monomer \( (R=2,5\text{-dibromo}) \) with the characterizing functional groups.
Figure II.10. The IR spectra of TSE monomer (R=3,5-dibromo) with the characterizing functional groups.
Appendix III. Monomer $^1$H-NMR Spectra

Figure III.1. The $^1$H NMR spectra of TSE monomer (R=2-acetyl)
Figure III.2. The $^1$H NMR spectra of TSE monomer (R=3-acetyl)
Figure III.3. The $^1$H NMR spectra of TSE monomer (R=2-3cyano).
Figure III.4. The $^1$H NMR spectra of TSE monomer (R= 4-dimethylamino)
FIGURE III.5. The $^1$H NMR spectra of TSE monomer (R = 4-diethylamino)
Figure III.6. The 1H NMR spectra of TSE monomer (R=2-iodo)
FIGURE III.7. The $^1$H NMR spectra of TSE monomer ($R$= 4-iodo)
Figure III.8. The $^1$H NMR spectra of TSE monomer (R=5-iodo-2-methoxy)
Figure III.9. The $^1$H NMR spectra of TSE monomer (R=2,5-dibromo)
Figure III.10. The $^1$H NMR spectra of TSE monomer ($R=3,5$-dibromo)
Appendix IV. Monomer $^{13}$C-NMR

Figure IV.1. The $^{13}$C NMR spectra of the TSE monomer (R = 2-acetyl)
Figure IV.2. The $^{13}$C NMR spectra of the TSE monomer (R = 3-acetyl)
Figure IV.3. The $^{13}$C NMR spectra of the TSE monomer (R=2-cyano)
Figure IV.4. The $^{13}$C NMR spectra of the TSE monomer ($R=4$-dimethylamino)
Figure IV.5. The $^{13}$C NMR spectra of the TSE monomer (R=2-
Figure IV.6. The $^{13}$C NMR spectra of the TSE monomer (R=4-iodo)
Figure IV.7. The $^{13}$C NMR spectra of the TSE monomer (R=3-iodo-4-methoxy)
Figure IV.8. The $^{13}$C NMR spectra of the TSE monomer (R = 5-iodo-2-
Figure IV.9. The $^{13}$C NMR spectra of the TSE monomer ($R=2',5'$-dibromo).
Figure IV.10. The $^{13}$C NMR spectra of the TSE monomer (R=3,5-dibromo)
Figure V.1. DSC Trace of ST-TSE copolymer (R=3-acetyl) with a $^\theta$ at 141°C.
Figure V.2. DSC Trace of ST-TSE copolymer (R=2-cyano) with a $T_g$ at 165°C.
Figure V.3. DSC trace of ST-TSE copolymer (R=4-dimethylamino) with Tg at 145°C.
Figure V.4. DSC Trace of ST-TSE copolymer (R=4-diethylamino) with a $T_g$ at 145°C.
Figure V.5. DSC Trace of ST-TSE copolymer (R=2-Iodo) with a Tg at 165°C.
Figure 8.6. DSC trace of ST-TSE copolymer (R=4-iodo) with a Tg at 185°C.
Figure V.7. DSC Trace of ST-TSE copolymer (R=3-iodo-4-methoxy) with a T_g at 167°C.
Figure V.8. DSC Trace of ST-TSE copolymer ($R=5$-iodo-2-methoxy) with a $T_g$ at 145°C.
Figure V.9. DSC Trace of ST-TSE copolymer (R=2,5-dibromo) with a $T_g$ at 173°C.
Figure V.10. DSC Trace of ST-TSE copolymer (R=3,5-dibromo) with a $T_g$ at 179°C.
Figure VI. The TGA trace of ST-TSE copolymer (R = 2-acety1) showing the decomposition of the copolymer in the green trace.
Figure VI.2. The TGA trace of ST-TSE copolymer (R=3-acetyl) showing the decomposition of the copolymer in the green trace.
Figure VI.3. The TGA trace of ST-TSE copolymer (R=2-cyano) showing the decomposition of the copolymer in the green trace.
Figure VI.4. The TGA trace of ST-TSE copolymer (R=4-dimethylamino) showing the decomposition of the copolymer in the green trace.
The copolymer in the green trace of Figure VI.5. The TGA trace of ST-TSE copolymer (R=2-iodo) showing the decomposition of the copolymer in the green trace.
Figure VI.6. The TGA trace of ST-1SE copolymer (R = 4-iodo) showing the decomposition of the copolymer in the green trace.
Figure VI.7. The TGA trace of ST-TSE copolymer (R= 3-iodo-4-methoxy) showing the decomposition of the copolymer in the green trace.
Figure VI.8. The TGA trace of ST-TSE copolymer (R=5-iodo-2-methoxy) showing the decomposition of the copolymer in the green trace.
Figure VI.9. The TGA trace of ST-TSE copolymer (R = 2,5-dibromo) showing the decomposition of the copolymer in the green trace.
Figure VI.10. The TGA trace of ST-TE copolymer (R = 3,5-dibromo) showing the decomposition of the copolymer in the green trace.
Appendix VII. Polymer GPC Chromatogram

**Figure VII.1** Gel Permeation Chromatogram of the average molecular weight distribution of the ST-TSE copolymer (R= 3-acetyl) with the average molecular weight at 17.3 kD
Figure VII.2 Gel Permeation Chromatogram of the average molecular weight distribution of the ST-TSE copolymer (R= 4-dimethylamino) with the average molecular weight at 9.5 kD
Figure VII.3 Gel Permeation Chromatogram of the average molecular weight distribution of the ST-TSE copolymer (R= 4-diethylamino) with the average molecular weight at 8.1 kD
Figure VII.4. Gel Permeation Chromatogram of the average molecular weight distribution of the ST-TSE copolymer (R= 2-iodo) with the average molecular weight 15.1 kD
**Figure VII.5.** Gel Permeation Chromatogram of the average molecular weight distribution of the ST-TSE copolymer (R= 7-iodo) with the average molecular weight 15.1 kD
Figure VII.6. Gel Permeation Chromatogram of the average molecular weight distribution of the ST-TSE copolymer (R= 3-iodo-4-methoxy) with the average molecular weight 24.0 kD
**Figure VII.7.** Gel Permeation Chromatogram of the average molecular weight distribution of the ST-TSE copolymer (R= 5-iodo-2-methoxy) with the average molecular weight 29.1 kD
Figure VII.8. Gel Permeation Chromatogram of the average molecular weight distribution of the ST-TSE copolymer (R= 2,5-dibromo) with the average molecular weight 13.4 kD
Figure VII.9. Gel Permeation Chromatogram of the average molecular weight distribution of the ST-TSE copolymer (R= 3,5-dibromo) with the average molecular weight 31.4 kD
Appendix VIII. Polymer IR Spectra

Figure VIII.1. The IR spectra of ST-TSE copolymer (R=2-acetyl) with the characterizing functional groups.

- CH stretch: 3050 cm⁻¹
- CN: 2249 cm⁻¹
- C=O: 1750 cm⁻¹
- Ring stretching: 1493 cm⁻¹
Figure VIII.2. The IR spectra of ST-TSE copolymer (R=3-acetyl) with the characterizing functional groups.
Figure VIII.3. The IR spectra of ST-TSE copolymer (R=2-cyano) with the characterizing functional groups.

The IR spectra show peaks at specific wavenumbers corresponding to different functional groups. The structure diagram illustrates the chemical composition of the copolymer, with peaks labeled for specific functional groups such as C=O, C-H stretch, and CN stretch at 1748 cm⁻¹, 2245 cm⁻¹, and 2950 cm⁻¹ respectively.
Figure VIII.4. The IR spectra of ST-TSE copolymer (R=4-dimethylamino) with the characterizing functional groups.
The IR spectra of ST-TSE copolymer (R = 2-iodo) with the characterizing functional groups.
Figure VIII.6. The IR spectra of ST-TSE copolymer (R=4-iodo) with the characterizing functional groups.
Figure VIII.7. The IR spectra of ST-TSE copolymer (R = 3-iodo-4-methoxy) with the characteristic functional groups.
Figure VIII.8. The IR spectra of ST-TSE copolymer (R = 5-iodo-2-methoxy) with the characterizing functional groups.

I 498 cm$^{-1}$: C=O; 1749 cm$^{-1}$: Ring stretching;
C 1220 cm$^{-1}$: C-H stretching; 3025 cm$^{-1}$.
Figure VIII.9. The IR spectra of ST-TSE copolymer (R=2,5-dibromo) with the characterizing functional groups.
Figure VIII.10. The IR spectra of ST-TSE copolymer (R=3’,5’-dibromomo) with the characterizing functional groups.
Appendix IX. Polymer $^1$H-NMR Spectra

Figure IX.1. $^1$H-NMR Spectra of ST-TSE Copolymer ($R=2$-acetyl)
Figure IX.2. $^1$H-NMR Spectra of ST-TSE Copolymer ($R=3$-acetyl)
Figure IX.3. $^1$H-NMR Spectra of ST-TSE Copolymer (R=4-dimethylamino)
Figure IX.4. $^1$H-NMR Spectra of ST-TSE Copolymer (R=4-diethylamino)
Figure IX.5. $^1$H-NMR Spectra of ST-TSE Copolymer (R=2-iodo)
Figure IX.6. 1H-NMR Spectra of ST-TSE Copolymer (R=4-iodo)
Figure IX.7. $^1$H-NMR Spectra of ST-TSE Copolymer (R=5-iodo-2-methoxy)
Figure IX.8. 1H-NMR Spectra of ST-TSE Copolymer (R=2,5-dibromo)
Figure IX.9. H-NMR Spectra of ST-TSE Copolymer (R=3,5-dibromo)