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Novel Copolymers of Trisubstituted Ethylenes and Styrene. 5. Dialkoxy Ring-Substituted Ethyl 2-Cyano-1-oxo-3-phenyl-2-propenylcarbamates

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Electrophilic trisubstituted ethylenes, dialkoxy ring-substituted ethyl 2-cyano-1-oxo-3-phenyl-2-propenylcarbamates, $RC_6H_4CH{=}C(CN)CONHCO_2C_2H_5$ (where R is 2,3-$(CH_3O)_2$, 2,4-$(CH_3O)_2$, 2,5-$(CH_3O)_2$, 3,4-$(CH_3O)_2$, 3,5-$(CH_3O)_2$, 3-C_2H_5O, 4-CH_3O), were prepared and copolymerized with styrene. The monomers were synthesized by the piperidine catalyzed Knoevenagel condensation of ring-substituted benzaldehydes and N-cyanoacetylurethane, and characterized by CHN analysis, IR, ^1H- and ^{13}C-NMR. All the ethylenes were copolymerized with styrene (M_1) in solution with radical initiation (ABCN) at 70°C. The compositions of the copolymers were calculated from nitrogen analysis and the structures were analyzed by IR, ^1H- and ^{13}C-NMR. The order of relative reactivity ($1/r_1$) for the monomers 2,3-$(CH_3O)_2$ = 2,4-$(CH_3O)_2$ (0.66) > 2,5-$(CH_3O)_2$ (0.61) > 3,5-$(CH_3O)_2$ (0.56) > 3,4-$(CH_3O)_2$ (0.56) > 3-C_2H_5O, 4-CH_3O (0.48). High T_g of the copolymers in comparison with that of polystyrene indicates decrease in chain mobility of the copolymer due to the high dipolar character of the trisubstituted ethylene structural unit. Decomposition of the copolymers in nitrogen occurred in two steps, first in 270–500°C range with a residue (3–7% wt.), which then decomposed in the 500–700°C range.

Keywords: Trisubstituted ethylenes, radical copolymerization, styrene copolymers

1 Introduction

Trisubstituted ethylenes (TSE, $CHR^1 = CR^2R^3$) continue to attract the attention of polymer chemists as reactive comonomers and as models for mechanistic studies. It was shown that electrophilic tri- and tetrasubstituted olefins are particularly useful in delineating the transition from radical to ionic chemistry (1). Previous studies showed that TSE containing substituents larger than fluorine have very low reactivity in radical homopolymerization of most tri- and tetrasubstituted olefins, their copolymerization with a monosubstituted alkene makes it possible to overcome these steric problems (2). Copolymerization of trisubstituted ethylenes, 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 acetate (7), vinyl ethers (8), methyl methacrylate (9), and *N*-vinyl-2-pyrrolidone (10).

In continuation of our studies of the monomer structure-reactivity correlation in the radical copolymerization of TSE monomers with carbamate group (11–13), we have prepared novel ring-substituted ethyl 2-cyano-1-oxo-3-phenyl-2-propenylcarbamates, $RC_6H_4CH{=}C(CN)CONHCO_2C_2H_5$ (where R is 2,3-$(CH_3O)_2$, 2,4-$(CH_3O)_2$, 2,5-$(CH_3O)_2$, 3,4-$(CH_3O)_2$, 3,5-$(CH_3O)_2$, 3-C_2H_5O, 4-CH_3O), and explore the feasibility of their copolymerization with styrene.

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, the glass transition temperatures (T_g) of the copolymers were measured with a TA (Thermal Analysis,

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Inc.) Model Q10 differential scanning calorimeter (DSC). The thermal scans were performed in the 25 to 200°C range at a heating rate of 10°C/min. T_g was taken as a midpoint of a straight line between the inflection of the peak's onset and endpoint. The thermal stability of the copolymers was measured by a thermogravimetric analyzer TA Model Q50 from ambient temperature to 700°C at 20°C/min. The molecular weights of the polymers were determined relative to polystyrene standards in THF solutions with sample concentrations 0.8% (wt/vol) by gel permeation chromatography (GPC) using a Altech 426 pump at an elution rate of 1.0 mL/min; TSK–GEL G4000H_{HR} column at 25°C, and Viscotek 302 and Viscotek UV 2501 detector. ^{1}H- and ^{13}C-NMR spectra were obtained on 10–25% (w/v) monomer or polymer solutions in $CDCl_3$ at ambient temperature using a Bruker 300 UltraShield spectrometer. Chemical shifts are reported referenced to TMS as 0 ppm. Proton spectra utilized 64 K data points with a sweep width of 31.4 kHz, a pulse delay of 5.3s and 12000 scans accumulated. Elemental analyses were performed by Quantitative Technologies Inc. (NJ).

2.2 Synthesis of Monomers

2,3-$(CH_3O)_2$, 2,4-$(CH_3O)_2$, 2,5-$(CH_3O)_2$, 3,4-$(CH_3O)_2$, 3,5-$(CH_3O)_2$, 3-C_2H_5O, 4-CH_3O–substituted benzaldehydes, *N*-cyanoacetylurethane, DMF, and piperidine supplied from Aldrich Chemical Co., were used for monomer synthesis as received. The preparation procedure was essentially the same for all the TSE monomers. In a typical synthesis, equimolar amounts of *N*-cyanoacetylurethane and an appropriate ring-substituted 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 recrystallization from methanol.

2.2.1. *Ethyl 2-Cyano-1-oxo-3-(2,3-dimethoxyphenyl)-2-propenylcarbamate*

Yield: 97.0%; mp 126°C; ^{1}H-NMR δ 8.8 (s, 1H, NH), 8.2 (s, 1H, CH=), 7.2, 7.8 (m, 3H, Ph), 4.3 (q, 2H, OCH_2), 3.9 (m, 6H, OCH_3), 1.4 (t, 3H, CH_3); ^{13}C-NMR δ 166, 152, 151, 150, 148, 127, 124, 127, 121, 117, 115, 105, 61, 60, 56, 15; IR 3290 (m, N—H), 2979 (m, C—H), 2218 (m, CN), 1757 (s, C=O), 1517 (C=C), 1186 (s, C—O), 794 (s, C—H out of plane). Anal. Calcd. for $C_{15}H_{16}N_2O_5$: C, 59.21%; H, 5.30%; N, 9.21%; Found: C, 58.94%; H, 5.40%; N, 9.19%.

2.2.2. *Ethyl 2-Cyano-1-oxo-3-(2,4-dimethoxyphenyl)-2-propenylcarbamate*

Yield: 82%; mp 153°C; ^{1}H-NMR δ 8.8 (s, 1H, NH), 8.2 (s, 1H, CH=), 6.5, 6.6, 8.2 (m, 3H, Ph), 4.3 (q, 2H, OCH_2), 3.9 (m, 6H, OCH_3), 1.3 (t, 3H, CH_3); ^{13}C-NMR δ 166, 162, 159, 150, 149, 131, 118, 114, 106, 98, 63, 56, 14; IR 3284 (N—H), 2982 (m, C—H), 2213 (m, CN), 1781 (s, C=O), 1575(C=C), 1161 (s, C—O), 775 (s, C—H out of plane). Anal. Calcd. for $C_{15}H_{16}N_2O_5$: C, 59.21%; H, 5.30%; N, 9.21%; Found: C, 59.18%; H, 5.31%; N, 9.21%.

2.2.3. *Ethyl 2-Cyano-1-oxo-3-(2,5-dimethoxyphenyl)-2-propenylcarbamate*

Yield: 67%; mp 121°C; ^{1}H-NMR δ 8.8 (s, 1H, NH), 8.4 (s, 1H, CH=), 6.7–7.7 (m, 3H, Ph), 4.2 (q, 2H, OCH_2), 3.9 (m, 6H, OCH_3), 1.3 (t, 3H, CH_3); ^{13}C-NMR δ 166, 152, 151, 150, 121, 118, 116, 115, 61, 56, 55, 51, 15; IR 3270 (N—H), 2981 (m, C—H), 2217 (m, CN), 1773 (s, C=O), 1508 (C=C), 1180 (s, C—O), 815, 775 (s, C—H out of plane). Anal. Calcd. for $C_{15}H_{16}N_2O_5$: C, 59.21%; H, 5.30%; N, 9.21%; Found: C, 58.83%; H, 5.28%; N, 9.21%.

2.2.4. *Ethyl 2-Cyano-1-oxo-3-(3,4-dimethoxyphenyl)-2-propenylcarbamate*

Yield: 86%; mp 164°C; ^{1}H-NMR δ 8.2 (s, 1H, NH), 7.7 (s, 1H, CH=), 7.0–7.5 (m, 3H, Ph), 4.3 (s, 2H, OCH_2), 4.0 (m, 6H, OCH_3), 1.4 (t, 3H, CH_3); ^{13}C-NMR δ 159, 156, 154, 150, 149, 128, 124, 117, 112, 111, 99, 63, 56, 14; IR 3339 (N—H), 2982 (m, C—H), 2207 (m, CN), 1758 (s, C=O), 1501 (C=C), 1280, 1147 (s, C—O), 849, 775 (s, C—H out of plane). Anal. Calcd. for $C_{15}H_{16}N_2O_5$: C, 59.21%; H, 5.30%; N, 9.21%; Found: C, 59.12%; H, 5.29%; N, 9.32%.

2.2.5. *Ethyl 2-Cyano-1-oxo-3-(3,5-dimethoxyphenyl)-2-propenylcarbamate*

Yield: 54%; mp 130°C; ^{1}H-NMR δ 8.3 (s, 1H, NH), 8.3 (s, 1H, CH=), 6.8–7.2 (m, 3H, Ph), 4.3 (q, 2H, OCH_2), 3.9 (m, 6H, OCH_3), 1.4 (t, 3H, CH_3);^{13}C-NMR δ 159, 158, 156, 150, 133, 131, 130, 125, 124, 120, 116, 104, 63, 14; IR 3227 (N—H), 2980 (m, C—H), 2215 (m, CN), 1760 (s, C=O), 1584 (C=C), 1193, 1158 (s, C—O), 830, 772 (s, C—H out of plane). Anal. Calcd. for $C_{15}H_{16}N_2O_5$: C, 59.21%; H, 5.30%; N, 9.21%; Found: C, 59.13%; H, 5.29%; N, 9.12%.

2.2.6. *Ethyl 2-Cyano-1-oxo-3-(3-ethoxy-4-methoxyphenyl)-2-propenylcarbamate*

Yield: 90.4%; mp 162°C; ^{1}H-NMR δ 8.4 (s, 1H, NH), 8.2 (s, 1H, CH=), 6.8–7.8 (m, 3H, Ph), 4.3 (s, 2H, Ph-OCH_2), 4.2 (m, 2H, OCH_2), 3.9 (s, 3H, $PhOCH_3$), 1.5 (t, 3H, $PhOCH_2C\underline{H}_3$), 1.4 (t, 3H, CH_3); ^{13}C-NMR δ 166, 154, 153, 151, 128, 123, 121, 115, 99, 65, 61, 15, 14; IR 3284 (N—H), 2987 (m, C—H), 2203 (m, CN), 1750 (s, C=O), 1508 (C=C), 1263, 1188 (s, C—O), 825, 771 (s, C—H out of plane). Anal. Calcd. for $C_{16}H_{18}N_2O_5$: C, 60.37%; H, 5.70%; N, 8.80%; Found: C, 60.15%; H, 5.67%; N, 8.71%.

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. 1,1′-Azobis(cyclohexanecarbonitrile) (ABCN) (Aldrich) was twice recrystallized from ethyl alcohol and then dried under reduced pressure at room temperature. Copolymers of the TSE monomers and styrene were prepared in 25-mL Pyrex screw cap ampoules at [ST]/[TSE] = 2 the monomer feed using 0.0045 mol/L of ABCN at an overall monomer concentration 2 mol/L in 20 mL of ethyl acetate. The copolymerization was conducted at 70°C. After a predetermined time the mixture was cooled to room temperature, and precipitated dropwise in methanol. The crude copolymers were purified by reprecipitation from chloroform solution into an excess of methanol. The composition of the copolymers was determined based on the nitrogen content.

4 Results and Discussion

4.1 Monomer Synthesis

The TSE monomers were synthesized by Knoevenagel condensation (14) of a ring-substituted benzaldehyde with an active hydrogen compound, N-cyanoacetylurethane, catalyzed by a base, piperidine.

$$RC_6H_4CHO + NCCH_2CONHCO_2C_2H_5 \rightarrow$$
$$RC_6H_4CH{=}C(CN)CONHCO_2C_2H_5$$

The condensation reaction proceeded smoothly, yielding crystalline products, which were purified by conventional techniques.

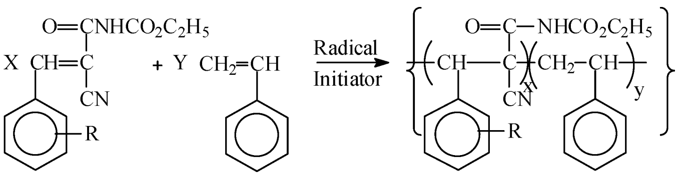
4.2 Homopolymerization

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. Inability of the monomers to polymerize is associated with steric difficulties encountered in the homopolymerization of 1,1- and 1,2-disubstituted ethylenes (2). 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.

4.3 Copolymerization

Copolymerization (Scheme 1) of the ring-substituted ethyl 2-cyano-1-oxo-3-phenyl-2-propenylcarbamates with ST resulted in formation of copolymers (Table 1) with weight-average molecular weights of 13.5 to 38.1 kD.

According to elemental analysis of the copolymers, between 37.3 and 42.1% of TSE monomer is present in the copolymers, which is indicative of significant reactivity of the monomers towards ST.



Sch. 1. Copolymer synthesis (where R is 2,3-$(CH_3O)_2$, 2,4-$(CH_3O)_2$, 2,5-$(CH_3O)_2$, 3,4-$(CH_3O)_2$, 3,5-$(CH_3O)_2$, 3-C_2H_5O, 4-CH_3O).

In an attempt to qualitatively correlate the observed monomer reactivities, we considered copolymer composition data obtained at [ST]/[TSE] = 2 monomer feed. The relative reactivity of ST in copolymerization with these monomers can be estimated by assuming applicability of the copolymer composition (Equation 1) of the terminal copolymerization model (2):

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

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 a TSE in the monomer feed, respectively. In the absence of the self-propagation of TSE monomers ($k_{22} = 0, r_2 = 0$), and at ($[M_1/[M_2] = 2$) monomer feed, Equation 1 yields Equation 2:

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

or the equation for the relative reactivity of styrene radical $k_{12}/\ k_{11}$ with TSE monomers, (Equation 3):

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

Consideration of monomer reactivities according to Equation 3 also involves the assumption of minimal copolymer compositional drift. This nonrigorous kinetic treatment nevertheless allows estimation of the reactivity of a styrene-ended polymer radical in reaction with electrophilic monomer (2). The order of relative reactivity ($1/r_1$) for the TSE monomers is 2,3-$(CH_3O)_2$ = 2,4-$(CH_3O)_2$ (0.66) > 2,5-$(CH_3O)_2$ (0.61) > 3,5-$(CH_3O)_2$ (0.56) > 3,4-$(CH_3O)_2$ (0.56) > 3-C_2H_5O, 4-CH_3O (0.48).

4.4 Structure and Properties

A comparison of the spectra of the monomers, copolymers and polystyrene shows, that the reaction between the TSE monomers and ST is a copolymerization. The structure of ST-TSE copolymers was characterized by IR and NMR spectroscopy. IR spectra of the copolymers show overlapping bands in 3700–3100, and 3100–2600 cm^1 region corresponding to N-H and C-H stretch vibrations, respectively. The bands for the TSE monomer unit are 2220–2275 (w, CN), 1652–1710 (s, C=O), and 1220–1270 cm^{-1} (m, C-O). Benzene rings of both monomers show ring stretching

Table 1. Copolymerization of styrene (M_1) and ring-substituted ethyl 2-cyano-1-oxo-3-phenyl-2-propenylcarbamates, $RC_6H_4CH{=}C(CN)CONHCO_2C_2H_5$ (M_2)

						TGA			
R	*Yield*[a], *Wt%*	*N wt%*	m_2 *in pol., mol %*	M_W, *kD*	T_g^b °*C*	*Onset of decomp.* °*C*	*10% wt. loss,* °*C*	*50% wt. loss,* °*C*	*Residue at 500* °*C, wt%*
2,3-$(CH_3O)_2$	13	3.86	41.9	13.5	175	284	330	355	7
2,4-$(CH_3O)_2$	19	3.87	42.1	23.0	160	286	326	362	3
2,5-$(CH_3O)_2$	36	3.73	40.5	26.2	144	281	321	369	4
3,4-$(CH_3O)_2$	23	3.56	38.7	38.1	178	287	325	376	3
3,5-$(CH_3O)_2$	19	3.58	38.9	38.0	184	286	323	368	3
3-C_2H_5O, 4-CH_3O	14	3.28	37.3	35.4	181	175	327	367	5

[a] Polymerization time was 5 h.
[b] T_g transition was observed by DSC.

bands at 1440–1495 and 1520–1596 cm^{-1} as well as a doublet 735–759, 695–710 cm^{-1}, associated with out-of-plane C-H bending motions. These bands can be readily identified in ST copolymers with TSE monomers containing cyano and carbonyl groups (10–12). The broadening of the NMR signals in the spectra of the copolymers is apparently associated with head-to-tail and head-to-head structures, which formed through the attack of a styrene-ended radical on both sides of TSE monomer (15). Thus ^{1}H-NMR spectrum of the styrene copolymer with ethyl 2-cyano-1-oxo-3-(3,5-dimethoxyphenyl)-2-propenylcarbamate (Figure 1) shows a broad peak in a 5.3–8.3 ppm region corresponding to phenyl protons. A double peak in a 3.3–4.3 ppm range is assigned to methoxy groups. Overlapping resonance in a 3.8–4.3 ppm range is assigned to methylene of the ethoxy group, similarly to one in the spectrum of *N*-cyanoacetylurethane. Absorption in 1.8–3.5 ppm region is assigned to ST backbone protons, methine and methylene, which are in close proximity cyano and urethane groups (15), and to the methine protons of a TSE unit in head-to-tail and head-to-head structures. Broad, overlapping resonances in the 0.8–2.2 ppm range are assigned to methine and methylene protons of ST monomer unit in the ST-TSE and ST-ST dyads. The ^{13}C-NMR spectra also support the suggested skeletal structure of the copolymers. Thus, the assignment of the peaks is as follows: 169

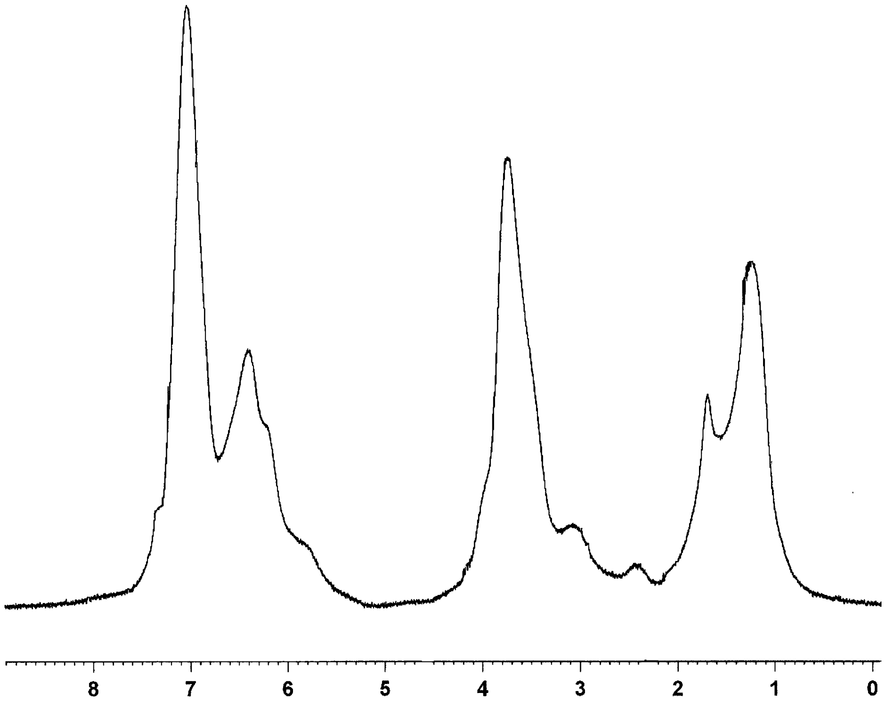


Fig 1. ^{1}H-NMR spectrum of styrene copolymer with ethyl 2-cyano-1-oxo-3-(3,5-dimethoxyphenyl)-2-propenylcarbamate in $CDCl_3$.

and 165 ppm (C=O), 148–135 ppm (quaternary carbons of both phenyls), 125–128 ppm (phenyl carbons), 112–113 ppm (CN), 50–60 ppm (methoxy, methine and quaternary carbons of TSE, and methylene carbon of ST), 40–44 ppm (ST methine), 32 ppm (OCH_2), and 24–26 ppm (methyl group). IR and NMR data showed that these are true copolymers, composed of both TSE and ST monomer units.

The copolymers prepared in the present work are all soluble in ethyl acetate, THF, DMF and $CHCl_3$ and insoluble in methanol, ethyl ether, and petroleum ether. They are amorphous and show no crystalline DSC endotherm. Relatively high T_g of the copolymers (Table 1) in comparison with that of polystyrene ($T_g = 95°C$) indicates decrease of chain mobility of the copolymer due to the high dipolar character of the TSE structural units.

Information on the degradation of the copolymers was obtained from thermogravimetric analysis. Decomposition of the copolymers in nitrogen occurred in two steps, first in 270–500°C range with a residue (3–7% wt.), which then decomposed in the 500–700°C range (Table 1). The decomposition products were not analyzed in this study, and the mechanism has yet to be investigated.

5 Conclusions

Novel electrophilic trisubstituted ethylenes, dialkoxy ring-substituted ethyl 2-cyano-1-oxo-3-phenyl-2-propenyl carbamates were prepared via a base catalyzed condensation of appropriate substituted benzaldehyde and N-cyanoacetylurethane. The copolymerization of the carbamates with styrene results in copolymers. The composition of the copolymers was calculated from nitrogen analysis and the structure was analyzed by IR, ^1H and ^{13}C-NMR. The order of relative reactivity ($1/r_1$) for the TSE monomers is 2,3-$(CH_3O)_2$ = 2,4-$(CH_3O)_2$ (0.66) > 2,5-$(CH_3O)_2$ (0.61) > 3,5-$(CH_3O)_2$ (0.56) > 3,4-$(CH_3O)_2$ (0.56) > 3-C_2H_5O, 4-CH_3O (0.48). High glass transition temperature of the copolymers in comparison with that of polystyrene indicates a substantial decrease in chain mobility of the copolymer due to the high dipolar character of the trisubstituted monomer unit. Decomposition of the copolymers in nitrogen occurred in two steps, first in 270–500°C range with a residue (3–7% wt.), which then decomposed in the 500–700°C range.

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