**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

# Radical Copolymerization of Fluorine Ring-Substituted 2-Phenyl-1,1-dicyanoethylenes with 4-Fluorostyrene: Synthesis and Characterization

Salima Atlas[a]; Mustapha Raihane[a]; Gregory B. Kharas[b]; Emi Hanawa[b]; Benjamin L. Hill[b]; Jessica D. Davis[b]; Amanda Mueller[b]
[a] Laboratory of Bioorganic and Macromolecular Chemistry, Chemistry Department, Faculty of Sciences and Techniques, Cadi Ayyad University, Marrakech, Morocco [b] Chemistry Department, DePaul University, Chicago, Illinois

**To cite this Article** Atlas, Salima , Raihane, Mustapha , Kharas, Gregory B. , Hanawa, Emi , Hill, Benjamin L. , Davis, Jessica D. and Mueller, Amanda(2010) 'Radical Copolymerization of Fluorine Ring-Substituted 2-Phenyl-1,1-dicyanoethylenes with 4-Fluorostyrene: Synthesis and Characterization', Journal of Macromolecular Science, Part A, 47: 6, 491 — 495

**To link to this Article: DOI:** 10.1080/10601321003741834

**URL:** http://dx.doi.org/10.1080/10601321003741834

*Journal of Macromolecular Science, Part A: Pure and Applied Chemistry* (2010) **47**, 491–495
Copyright © Taylor & Francis Group, LLC
ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601321003741834

# Radical Copolymerization of Fluorine Ring-Substituted 2-Phenyl-1,1-dicyanoethylenes with 4-Fluorostyrene: Synthesis and Characterization

SALIMA ATLAS[1], MUSTAPHA RAIHANE[1], GREGORY B. KHARAS,[2,*] EMI HANAWA[2],
BENJAMIN L. HILL[2], JESSICA D. DAVIS[2] and AMANDA MUELLER[2]

[1] *Laboratory of Bioorganic and Macromolecular Chemistry, Chemistry Department, Faculty of Sciences and Techniques, Cadi Ayyad University, Marrakech, Morocco*
[2] *Chemistry Department, DePaul University, Chicago, Illinois*

Received, Accepted January 2010

Novel copolymers of trisubstituted ethylene monomers, fluorine ring-substituted 2-phenyl-1,1-dicyanoethenes, $RC_6H_4CH{=}C(CN)_2$ (where R is 2-F, 3-F, and 4-F) and 4-fluorostyrene were prepared at equimolar monomer feed composition by solution copolymerization in the presence of a radical initiator (ABCN) at 70°C. The composition of the copolymers was calculated from nitrogen analysis, and the structures were analyzed by IR, $^1$H and $^{13}$C-NMR. High $T_g$ of the copolymers, in comparison with that of poly(4-fluorostyrene) indicates a substantial decrease in chain mobility of the copolymer due to the high dipolar character of the trisubstituted ethylene monomer unit. The gravimetric analysis indicated that the copolymers decomposed in two stages in the range 210–600°C.

**Keywords:** Trisubstituted ethylenes, radical copolymerization, 4-fluorostyrene copolymers

## 1 Introduction

Trisubstituted ethylenes (TSE, $CHR^1 = CR^2R^3$) continue to attract attention of polymer chemists as reactive comonomers and models for mechanistic studies. It was shown that electrophilic tri- and tetrasubstituted 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 tetrasubstituted 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 electric applications of cyano polymers, strong piezoelectric activity was observed in the alternating copolymer of 1,1-dicyanoethylene (vinylidene cyanide) (VCN) and vinyl acetate (VAc) by Miyata et al. (10). The rolled and polarized copolymer showed piezoelectricity strong enough to be comparable to that in poly(vinylidene fluoride) films treated under the same poling conditions, which was explained by the introduction of oriented C-CN groups. Large dielectric relaxations in a poly(VCN-alt-VAc) were observed by Furukawa et al. (11). This copolymer has impedance similar to that of the human body and has been suggested for medical applications as an ultrasonic transducer (12). Dielectric behavior of TSE copolymers of vinylidene methyl cyanide with 4-fluorostyrene and 4-chlorostyrene has been studied (13). The $\alpha$ relaxation phenomena have been characterized around $T_g$ temperatures. The low values of $\Delta\varepsilon$ were explained by the steric effect of the bulky aromatic groups. Montheard et al. (14) have studied the radical copolymerization of VCN with two styrenic comonomers bearing a fluorinated chain in the para position, leading to alternating copolymers. A synthesis (15) and a study of dielectric behavior (16) of TSE copolymer based on vinylidene methyl cyanide and 2,2,2-trifluoroethyl methacrylate have been reported.

---

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

Recently, we have reported synthesis and characterization of copolymers of 2-phenyl-1,1-dicyanoethylene with 4-fluorostyrene and pentafluorostyrene (17).

In continuation of our studies of the monomer structure-reactivity correlation in the radical copolymerization of electrophilic trisubstituted ethylene monomers and in order to develop new dielectric fluoronitrile polymers containing C–CN and C–F substituents with strong dipole moments, we describe in this paper the synthesis and characterization of TSE copolymers of 4-fluorostyrene with fluorine ring-substituted 2-phenyl-1,1-dicyanoethylenes.

## 2 Experimental

### 2.1 Materials

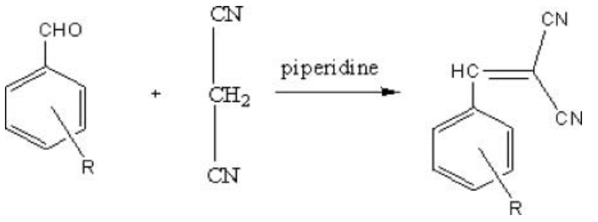
2-Fluoro, 3-fluoro, and 4-fluorobenzaldehyde, piperidine, 4-fluorostyrene (4FST), 1,1′-azobis(cyclohexanecarbonitrile) (ABCN), petroleum ether, chloroform and toluene supplied from Aldrich Chemical Co., were used as received.

### 2.2 General Procedures

Infrared spectra of the TSE monomers and polymers (KBr plates) were determined with a Nicolet Avatar 360 FT-IR spectrometer. The melting points of the monomers and the glass transition temperatures ($T_g$) of the copolymers were measured with TA (Thermal Analysis, Inc.) Model Q10 differential scanning calorimeters (DSC). The thermal scans were performed in a 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 thermogravimetric analyzer TA Q50 from ambient temperature to 800°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 G4000$H_{HR}$ column at 25°C, 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 Avance 300 MHz spectrometer. Elemental analyses were performed by Quantitative Technologies Inc. (NJ).

### 2.3 Monomer Synthesis

The fluorine ring-substituted 2-phenyl-1,1-dicyanoethenes were prepared by Knoevenagel condensation (18) (Scheme 1). The synthesis procedure and characterization of the TSE monomers was described earlier (19, 20). In a typical synthesis, equimolar amounts of malononitrile and an appropriate benzaldehyde were mixed with 2 mL 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, purified by crystallization from 2-propanol, and dried until constant weight in a vacuum oven at ambient temperature.



**Sch. 1.** Monomer synthesis (where R = 2F, 3F, and 4F).

## 3 Result and Discussion

### 3.1 Homopolymerization

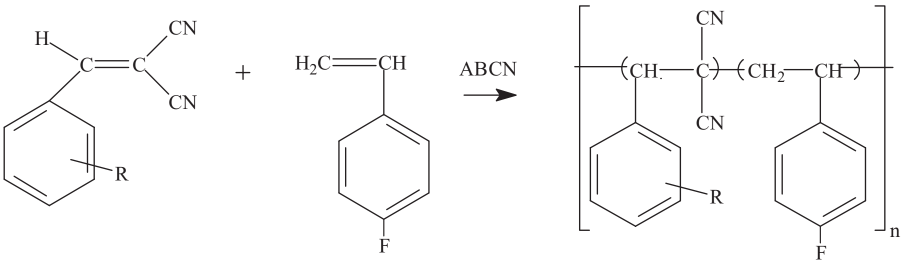
An attempted homopolymerization of the TSE monomers in the presence of ABCN did not produce any polymer as indicated by the lack of a precipitate in methanol. Inability of TSE to polymerize is associated with steric difficulties encountered in homopolymerization of 1,1- and 1,2-disubstituted ethylenes (2). Homopolymerization of 4FST under conditions identical to those in the copolymerization experiments yielded homopolymers (Table 1).

### 3.2 Copolymerization

Copolymers of the TSE monomers and 4FST were prepared in 25-ml glass screw cap vials at 4FST/TSE=1/1 molar ratio of monomer feed in toluene at 70°C using ABCN as an initiator (Scheme 2). After a predetermined time, the mixture was cooled to the room temperature, and precipitated dropwise in petroleum ether. The crude copolymers were purified by re-precipitation from chloroform solution into an excess of petroleum ether. Then copolymers were dried in a vacuum oven at 70°C until constant weight. The composition of the copolymers was determined based on the nitrogen content (Table 1).

### 3.3 Structure and Properties

The structure of TSE-4FST copolymers was characterized by IR and NMR spectroscopy. The IR absorption spectra of the copolymers showed characteristic bands for both TSE and 4FST units. Vinylic bond absorbances (C=C) of TSE and 4FST at 1615 and 1618 cm$^{-1}$, respectively, are absent, indicating that the copolymerization reaction has occurred. These spectra showed the appearance of a weak peak corresponding to the cyano group absorption of TSE at 2230–2240 cm$^{-1}$; which is observed in all cyano copolymers. Benzene rings of both comonomers show stretching bands at 1610, 1514 and 1453 cm$^{-1}$, as well as a doublet



**Sch. 2.** Copolymers synthesis (where R = 2-F, 3-F, and 4-F).

930, 834 $cm^{-1}$, associated to C-H out of plane deformations. Similar result was observed for the IR spectrum of 2-Phenyl-1,1-dicyanoethene with 4FST (17).

Figure 1 shows $^1H$-NMR spectrum of copolymer of 2-(3-Fluorophenyl)-1,1-dicyanoethylene and 4-fluorostyrene. The broadening of the NMR signals in the spectra of the copolymer is apparently associated with head-to-tail (A) and head-to-head (B) structures, which formed through the attack of 4-fluorostyrene ended radical on both sides of TSE monomer units. The presence of A and B configurations structures was observed in the copolymers of styrene and 2-phenyl-1,1-Dicyanoethene (21). The $^1H$-NMR spectra show a broad signal of TSE and 4FST aromatic protons at 6.0-8.0 ppm which result from overlapping multiplets of four spin system. The resonance at 4.0–3.4 ppm is assigned to the styrenic backbone protons, methylene in structure (A) and methine in structures (B) which are in close proximity to cyano groups in TSE-4FST diads or in 4FST centered TSE-4FST-TSE triads. The resonance in the range 2.6–3.3 ppm is assigned to the methine protons of fluorinated TSE monomers in structures (A) and (B). This assignment is based on the comparison with the methine proton absorption in head-to-head and head-to-tail copolymers (21). The overlapping resonances in the 0.8–2.0 ppm range are attributed to the methine protons of 4FST-4FST dyads.

The $^{13}C$-NMR spectra also support the suggested skeletal structure of the copolymers. The $^{13}C$-NMR spectrum of 2-(3-fluorophenyl)-1,1-dicyanoethylene-4-fluorostyrene copolymer is shown in Figure 2. Based on comparison of the $^{13}C$-NMR chemical shifts in the spectra of poly(4-fluorostyrene), and copolymers of 2-phenyl-1,1-dicyanoethylene and 4-fluorostyrene (17), the assignments of peaks are as follows : 158–168 ppm (phenyl carbons bonded to fluorine atoms of TSE and 4FST), 121–139 ppm (phenyl carbons), 110–120 ppm (CN) of TSE unit and 32–50 ppm (methine and methylene backborne carbons of TSE and 4FST). The absorption at 58 ppm is assigned to the quaternary carbon of TSE ($\underline{C}(CN)_2$). In addition, we noted also the absence of the vinylic bond at 159 ppm (=CH) and 83 ppm (=C) associated to TSE monomers. The IR and NMR data showed that these are true copolymers, composed of 4FST and TSE monomer units. The composition of the fluorine ring-substituted of the TSE-4FST copolymers can be calculated by measuring integrals of some characteristic peaks in $^{13}C$-NMR spectra. For example, in the range 158-168 ppm of $^{13}C$-NMR of 2-(3-fluorophenyl)-1,1-dicyanoethylene and 4FST copolymer (Fig. 2), the areas of the signals of the quaternary carbons F-$C_3$ of TSE ($I_1$) at 164 and F-$C_4$ of 4FST ($I_2$) at 161 ppm show that the calculated percentage of TSE in the copolymer using equation below, is close to 41.6%:

$$\text{TSE mol\%} = \frac{I_1}{I_1 + I_2} \times 100$$

The result is in good agreement with that determined from elemental analysis (%N=8.03, 41.8%) for this copolymer (Table 1).

The copolymers prepared in the present work are all soluble in ethyl acetate, DMF, $CHCl_3$ and insoluble in petroleum ether, and heptane. The copolymerization of the

**Table 1.** Copolymerization of 4-fluorostyrene ($M_1$) and fluoro ring-substituted 1,1-dicyanoethylenes, $RC_6H_4CH{=}C(CN)_2$ ($M_2$)

| | | | | | | *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-F | 38 | 8.22 | 41.9 | 5.9 | 148 | 210 | 287 | 322 | 6 |
| 3-F | 71 | 8.03 | 40.8 | 7.7 | 163 | 240 | 296 | 328 | 8 |
| 4-F | 71 | 6.48 | 31.9 | 5.3 | 140 | 220 | 295 | 347 | 7 |

[a] Polymerization time was 24 h.

[b] $T_g$ transition was observed by DSC.

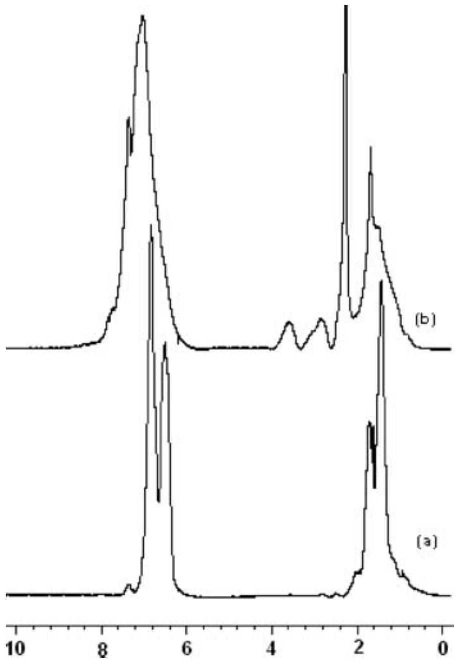


**Fig. 1.** $^1$H-NMR spectra of Poly(4-Fluorostyrene) (a) and Copolymer of 2-(3-Fluorophenyl)-1,1-dicyanoethylene and 4-Fluorostyrene (b).

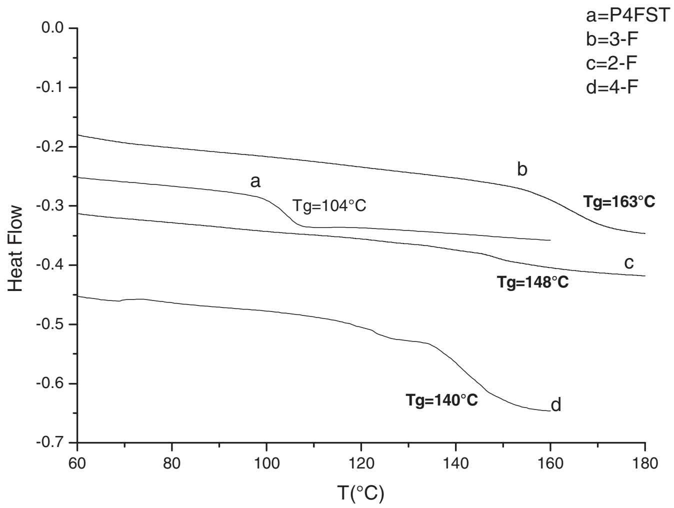


**Fig. 3.** DSC traces of TSE-4FST copolymers and poly(4-fluorostyrene).

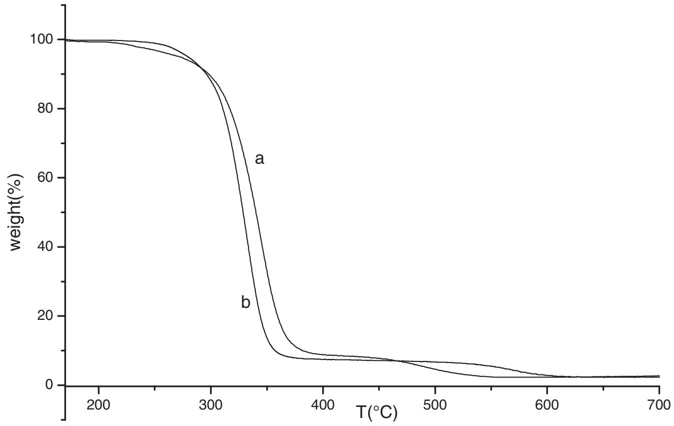


**Fig. 4.** TGA traces of TSE-4FST copolymers (a) 4-F and (b) 3-F.

fluorine ring-substituted TSE with 4-fluorostyrene results in formation of copolymers with molecular weight average ($M_w$) from 5200 to 7800 Daltons.

Two key thermal properties, glass transition temperature, $T_g$, and thermal degradation were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. All the synthesized copolymers show a transition from glassy state to viscoelastic state (Fig. 3). The copolymers show no crystalline DSC endotherm thus suggesting amorphous behavior. Relatively high $T_g$ of the copolymers (Table 1) in comparison with that of poly(4-fluorostyrene) ($T_g = 104°C$) indicates a 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 in nitrogen. The decomposition products were not analyzed in this study, and the mechanism has yet to be investigated. Figure 4 shows the TGA traces of the thermal degradation of the copolymers of 4FST and fluorine ring-substituted of 2-phenyl-1,1-dicyanoethylene copolymers in nitrogen. Results of analyses summarized in Table 1. Figure 4 shows

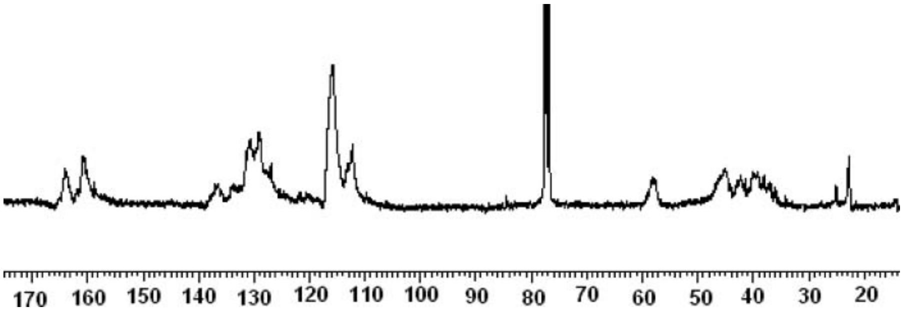


**Fig. 2.** $^{13}$C-NMR spectrum of Copolymer of 2-(3-Fluorophenyl)-1,1-dicyanoethylene and 4-Fluorostyrene.

that the copolymers begin to degrade in the 210–240°C range. The decomposition occurred in two steps, with rapid decomposition in the 210–400°C range followed by slow second stage decomposition in the 400–600°C range.

## 4 Conclusions

Copolymerization of fluorine ring-substituted 2-phenyl-1,1-dicyanoethylene (TSE) with 4-fluorostyrene in solution with radical initiation (ABCN) at 70°C yielded random copolymers with TSE alternating units. The composition of the copolymers was calculated from nitrogen analysis and the structure was analyzed by IR, $^{1}$H- and $^{13}$C-NMR. Higher glass transition temperature of the copolymers in comparison with that of poly(4-fluorostyrene) indicates a decrease in chain mobility of the copolymer due to the high dipolar character of the trisubstituted ethylene monomer unit. The gravimetric analysis indicated that the copolymers decomposed in two stages in the range 210–600°C. The study of dielectric behavior of these copolymers is under investigation.

## Acknowledgments

We are grateful that the project is supported by the CNRST of Morocco for the framework of cooperation Morocco-USA in the field of Material (n° 87/2007: Materials World Network).

We are grateful to acknowledge that the project is partly supported by the National Science Foundation Polymer Program (DMR-0710520), Coatings Industry Education Foundation (CIEF), Chicago Society of Coatings Technology, the DePaul University Research Council, and Office of Sponsored Programs and Research. E. Hanawa and B.L. Hill were supported by the CIEF graduate fellowship.

## References

1. Hall, H.K., Jr. and Padias, A.B. (2004) *J. Polym. Sci. Part A: Polym. Chem.*, 42, 2845–2858.
2. Odian, G. *Principles of Polymerization, 4th* Ed.; Wiley: New York, 2004.
3. Hall, H.K., Jr. and Daly, R.C. (1975) *Macromolecules.*, 8, 22–31.
4. Hall, H.K., Jr. and Ykman, P. (1977) *Macromolecules.*, 10, 464–469.
5. Kharas, G.B. (1996) Trisubstituted ethylene copolymers. In *Polymeric Materials Encyclopedia*, edited by Salamone, J.C., CRC Press: Boca Raton, Vol. 11, 8405–8409.
6. Kreisel, M., Garbatski, U. and Kohn, D.H. (1964) *J. Polym. Sci.,* 2(1; Part A) 105–121.
7. Kharas, G.B. and Ajbani, H. (1993) *J. Polym. Sci.*, A31, 2295–2303.
8. Sayyah, S.M., El-Shafiey, Z.A., El-Sockary, M.A. and Kandil, U.F. (2002) *Int. J. Polym. Mat.*, 51(3), 225–242.
9. Kharas, G.B. (1988) *J. Appl. Polym. Sci.*, 35, 733–741.
10. Miyata, S., Yoshikawa, M., Tasaka, S. and Ko, M. (1980) *Polymer J.*, 12 (12), 857–60.
11. Furukawa, T., Date, M., Nakajima, K., Kosaka, T. and Seo, I. (1986) *Jpn J of App Phys*., 25, 1178–82.
12. Tasaka, S., Miyasato, K., Yoshikawa, M., Miyata, S. and Ko, M. (1984) *Ferroelectrics.*, 57, 267.
13. Raihane, M., Montheard, J. P. and Boiteux, G. (2000) *Macromol. Chem. Phy.*, 17, 2365–2370.
14. Montheard, J-P., Zerroukhi, A., Ouillon, I., Boinon, B. and Pham, Q-T. (1995) *Macromol. Rep.*, *A*32(Suppl. 1 and 2), 1–11.
15. Raihane, M. and Ameduri, B. (2006) *J. Fluor. Chem*., 127, 391–399.
16. Meskini, A., Raihane, M., Ameduri, B., Hakme, C., Sage, D., Stevenson, I., Boiteux, G., Seytre, G. and Kaddami, H. (2009) *Eur. Poly. J.*, 45(3), 804–812.
17. Kharas G.B., Hanawa E., Hill L.B., Atlas S. and Raihane M. (2009) *J. Macromol. Sci*, *Part A.*, 46, 1–6.
18. Smith, M.B. and March, J. (2001) Addition to Carbon-Hetero Multiple Bonds. In *March's Advanced Organic Chemistry*: J. Wiley & Sons: New York Ch. 16, 1225.
19. Kharas G.B., Russell S. M., Ward D.R., Doshi R.M., Hijazin. M.Y., Korkofigas. E., Kuzenkova. N., Leung B., Merchant F.A., Merchbach N.T. and Opiola E.S. (2008) *J. Macromol. Sci, Part A.*, 45, 2133–136.
20. Kharas, G.B., Karas J.W., Michna V.K., Grajzer K., Karins K.A., Kontzias C., Rothacker E.P., McManigal K.A., Dian B.C. and Watson K. (2001) *J. Macromol. Sci, Part A.,* 38(9), 889–896.
21. Kharas, G.B., Murau, P.A., Watson, K. and Harwood, H.J. (1992) *Polym. Int.,* 28, 67-74.