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# Functional styrenic copolymer based on 2-(dimethylamino)ethyl methacrylate: Reactivity ratios, biological activity thermal properties and semi-conducting properties

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ABSTRACT

A new type of styrene monomer, 1-[(4-ethenylbenzyl)oxy]-2,3,4,5,6-pentafluorobenzene (EBOPFB) was synthesized. The free-radical-initiated copolymerization of EBOPFB with 2-(dimethylamino)ethyl methacrylate(DMAEMA) were carried out in 1,4-dioxane solution at 65 °C using 2,2′-azobisisobutyronitrile (AIBN) as an initiator with different monomer-to-monomer ratios in the feed. The copolymers were characterized by FTIR, $^{1}H$ and $^{13}C$-NMR spectral studies. The analysis of reactivity ratios revealed that DMAEMA is less reactive than EBOPFB, and copolymers formed are statistically in nature. Thermogravimetric analysis of the polymers reveals that the thermal stability of the copolymers increases with an increase in the mole fraction of EBOPFB in the copolymers. Glass transition temperatures of the copolymers were found to decrease with an increase in the mole fraction of DMAEMA in the copolymers. The room temperature conductivity values of this polymer increases with DMAEMA unit in the copolymer and varies 2.8 and 3.9 $\times 10^{-8}$ S/cm.



## 1. Introduction

In polymer science, the improvement of the mechanical properties of polymers has been accepted as interesting, but today the interesting of special electrical and optical properties of polymers are increasing. The use of raw materials from renewable sources has been the focusing of the attention of a great number of scientific research groups through all over the world during the last three decades. Nowadays, a strong demand exists for "functional polymers" with very specific properties. Functional groups give to polymer structure a special character substantially different from the inherent properties of the basic polymer chain [1]. In recent years some comprehensive works have been published on functional monomers and their polymers [2–4].

Fluorine-containing polymers are particularly attractive and useful compounds because of their unique properties including high thermal, chemical, aging and weather resistance; low dielectric constants, refractive index, surface energy and flammability; excellent inertness to solvents, hydrocarbons, acids, alkalis and moisture adsorption as well as interesting oil and water repellency due to the low polarizability and the strong electronegativity of the fluorine atom [5–7]. Consequently, fluorine-containing polymers have wide applications in modern technologies ranging from building, automotive and aerospace industries to optics and microelectronics [8,9].

Styrene is a widely used industrial chemical and its polymers are used in plastics, latex paints and coatings, synthetic rubbers, polyesters and styrene alkyd coatings. Styrene is present in food and the environment. However, styrene and its metabolites are known to have serious negative effects on human health [10,11]; therefore, before discharge to the environment, both the liquid and gaseous effluents of petrochemical complexes should undergo an appropriate treatment to decrease the concentration of styrene to below toxic levels.

Poly(DMAEMA) is a useful carrier for non-viral gene delivery since its cationic charges can condense plasmid DNA by ion interactions [12]. Poly(DMAEMA) based block copolymers can be cross-linked to form nanospheres with a cross-linked shell, which can then act as nanoreactors and drug delivery vehicles [13]. Poly(DMAEMA) has indeed gained popularity due to a higher cellular permeability combined with a lower cytotoxicity [14–16]. Although efficient as carriers, several of these polymers can cause severe in vitro and in vivo toxicity [17–19].

EBOPFB is also new styrenic monomer having pendant fluorine atom. In previous studies, the synthesis, characterization and thermal behavior of similarly monomers and their polymers

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have been described [20]. However, the studies on reactivity ratios in the copolymerizations of EBOPFB with DMAEMA are not appearing in the literature. It is thought that styrene polymers bearing a important group such as fluorine and their copolymerization behavior acts will be interesting for polymer chemistry. The present article investigates the synthesis, structural, and thermal characterization of copolymers of EBOPFB with DMAEMA as well as the determination of reactivity ratios in the copolymerization. The biological activities and activation energies of the copolymers were also obtained. Reactivity ratios for the classical copolymerization model were determined using the linearization methods of Finemann–Ross (FR method) and Kelen–Tüdös (KT method) [21,22].

## 2. Result and discussion

### 2.1. Characterization of the copolymers

The copolymerization of EBOPFB with DMAEMA in 1,4-dioxane solution was studied in a wide composition interval with the mole fractions of EBOPFB ranging from 0.2 to 0.8 in the feed. The reaction time was selected in trials to give conversions less than 10% in order to satisfy the differential copolymerization equation. The amounts of monomeric units in the copolymers were determined by elemental analysis benefiting from N content of DMAEMA units (Table 1).

### 2.2. Solubility parameters

The solubility parameters of the polymers were determined by using a titration method [23] at 25 °C from a solubility test using $CH_2Cl_2$ as a solvent and *n*-hexane and ethanol as non-solvent. The polymers were soluble in chloroform, dimethylformamide, dimethylsulfoxide, tetrahydrofuran, dichloromethane, and 1,4-dioxane but insoluble in *n*-hexane, *n*-heptane, hydroxyl group containing solvent such as methanol and ethanol. The solubility parameters values of the copolymers are between 9.47 and 10.83 $(cal/cm^3)^{1/2}$. These values are close to 9.90 $(cal/cm^3)^{1/2}$ which is 1,4-dioxane solubility parameter. The THF is the best solvent for all of the copolymers. The solubility parameters ($\delta$) values are presented in Table 1.

### 2.3. Spectroscopic characterization

The FTIR spectrum of the copolymer shows characteristic band at 1735 $cm^{-1}$ (–C=O stretching in the DMAEMA units) is the most for the copolymer. The peak at 3050 $cm^{-1}$ corresponds to the C–H stretching of the aromatic system. The symmetrical and asymmetrical stretching due to the methyl and methylene groups have been observed at 1985, 2940, and 2865 $cm^{-1}$. The ring breathing vibrations of the aromatic nuclei have been observed at 1600, 1505, and 1470 $cm^{-1}$. The asymmetrical and symmetrical bending vibrations of methyl groups have been seen at 1455 and 1380 $cm^{-1}$. The C–H and C–C out-of-plane bending vibrations of the aromatic nuclei have been observed at 790 and 565 $cm^{-1}$, respectively [24]. The $^1$H-NMR and $^{13}$C-NMR spectrums of the poly(EBOPFB-co-DMAEMA) [0.53:0.47] are shown in Fig. 1. The $^1$HNMR and $^{13}$C-NMR spectrum of copolymer has the characteristic resonances corresponding to the general formula. All chemical shift data are also in agreement with the given molecular structure shown in Fig. 1.

### 2.4. Glass transition temperatures

The glass transition ($T_g$) temperatures were determined by a Shimadzu 60H DSC. Samples of about 5–8 mg held in sealed aluminum crucibles and the heating rate of 10 °C/min under a dynamic nitrogen flow (5 l $h^{-1}$) were used for the measurements. From DSC measurements $T_g$ was taken as the midpoint of the transition region. The $T_g$ of poly(EBOPFB) is 65 °C, and that poly(DMAEMA) is 19 °C. In comparison to that of poly(DMAEMA), the shift to higher temperature is also noted for all the copolymers studied and its magnitude is dependent on the increasing in EBOPFB molar fraction in the copolymer chain. An increase in $T_g$ of copolymers may be due to the introduction of EBOPFB into DMAEMA in comonomer, which increases the inter-molecular polar interactions among the molecular chains due to structure stretching. It can be seen that the observed $T_g$ increases with increasing EBOPFB and presents a striking positive deviation with respect to linearity, which can be associated with a lower free volume, mobility and flexibility than a mixture of DMAEMA and EBOPFB units. The variation of $T_g$ of copolymers with mole fraction of the EBOPFB unit in the copolymer is shown in Fig. 2.

The thermal properties of the copolymers are influenced by their chemical structure and composition and the monomer sequence distributions. Several relationships have been employed to describe the effect of these parameters on the glass transition temperature of the copolymers. The simplest equation describing the effect of composition on $T_g$ is the Gibbs–Di Marzio equation [25]:

$$T_g = \Phi_{\mathrm{EBOPFB}} T_{g_{\mathrm{DMAEMA}}} + \Phi_{\mathrm{EBOPFB}} T_{g_{\mathrm{DMAEMA}}} \quad (1)$$

where $\Phi_{\mathrm{EBOPFB}}$, $\Phi_{\mathrm{DMAEMA}}$ are the mole fractions of EBOPFB and DMAEMA monomers respectively in the copolymer and $T_{g_{\mathrm{EBOPFB}}}$, $T_{g_{\mathrm{DMAEMA}}}$ the glass transition temperatures of the two homopolymers respectively.

A similar relationship was introduced by Fox [26]:

$$\frac{1}{T_g} = \frac{W_{\mathrm{EBOPFB}}}{T_{g_{\mathrm{EBOPFB}}}} + \frac{W_{\mathrm{DMAEMA}}}{T_{g_{\mathrm{DMAEMA}}}} \quad (2)$$

**Table 1**
Monomer compositions in feed and in the copolymer.

| Sample | Feed composition (mol fraction) | | Conv. (%) | $t$ (min) | N% | $\delta$ $(cal/cm^3)^{1/2}$ | Copolymer composition (mol fraction) | |
|---|---|---|---|---|---|---|---|---|
| | EBOPFB ($M_1$) | DMAEMA ($M_2$) | | | | | EBOPFB ($m_1$) | DMAEMA ($m_2$) |
| 1 | 0.20 | 0.80 | 8.50 | 45 | 4.35 | 9.47 | 0.35 | 0.65 |
| 2 | 0.30 | 0.70 | 9.50 | 60 | 3.39 | 9.62 | 0.46 | 0.54 |
| 3 | 0.40 | 0.60 | 9.90 | 75 | 3.19 | 9.81 | 0.49 | 0.51 |
| 4 | 0.50 | 0.50 | 8.90 | 90 | 2.80 | 9.98 | 0.53 | 0.47 |
| 5 | 0.60 | 0.40 | 9.25 | 105 | 2.47 | 10.25 | 0.58 | 0.42 |
| 6 | 0.70 | 0.30 | 9.50 | 120 | 1.93 | 10.75 | 0.66 | 0.34 |
| 7 | 0.80 | 0.20 | 9.80 | 135 | 1.27 | 10.83 | 0.75 | 0.25 |

Polymerization was carried out in 1,4-dioxane solution at 65 °C.