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Microstructure determination of 9-ethyl-3-hydroxymethylcarbazolyl acrylate/methacrylonitrile using two-dimensional NMR spectroscopy

Ajaib Singh Brar *, Sonia Gandhi

Department of Chemistry, Indian Institute of Technology, Delhi, Hauz Khas, New Delhi 110016, India

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Abstract

Solution polymerization was carried out using AIBN as initiator at 60 °C and varying the molar infeed ratio to get different composition of 9-ethyl-3-hydroxymethylcarbazolyl acrylate-co-methacrylonitrile (C/N). The molecular weight was determined using gel-permeation chromatography (GPC). Differential scanning calorimetry (DSC) was used to determine the glass transition temperature (T_g). $^{13}C\{^1H\}$, DEPT-45, 90 and 135 NMR techniques were used to distinguish the α-methyl, methine, backbone methylene and quaternary carbon resonance signals of C/N copolymers. Correlation of 1D (^1H, $^{13}C\{^1H\}$, DEPT) and 2D (HSQC, TOCSY, HMBC) NMR data were used to completely assign various overlapping and broad signals of C/N copolymers. Heteronuclear multi bond correlation (HMBC) studies were used to completely assign various nitrile resonances. The reactivity ratios calculated by Kelen–Tudos (KT) method were found to be $r_C = 0.31 \pm 0.03$ and $r_N = 0.80 \pm 0.02$ whereas those calculated from RREVM method were found to be $r_C = 0.35$ and $r_N = 0.83$, respectively.

Keywords: NMR; Microstructure; Photorefractive polymers; 9-Ethyl-3-hydroxymethylcarbazolyl acrylate

1. Introduction

Carbazole-based polymers have attracted much attention due to its potential applications as photorefractive materials [1–6]. These polymers possess optical properties [7–10] and good hole transporting ability in light-emitting devices [11] owing to its photoconducting and electro-optical properties [12–19], which in turn are essential properties needed for a material to be photorefractive. Photorefractive properties are possessed by these kinds of copolymers due to photoconductivity combined with non-linear optical activity (NLO). Photorefractivity is enhanced in the copolymers containing ring substituted carbazolyl pendant group due to the generation of charge carriers via intramolecular charge transfer complex [20–22]. The NLO response makes these copolymers interesting for several applications in the field of optical communication, optical switching and optical signal processing. 9-Ethyl-3-hydroxymethylcarbazolyl acrylate-co-methacrylonitrile (C/N) is the copolymer belonging to this class of photorefractive materials.

Copolymerization with electron acceptor monomers such as methacrylonitrile can be used as a tool to improve the physical, chemical and optical properties of these copolymers [23,24]. Enhancement of non-linear optical response is achieved when these electron acceptor groups are copolymerized with carbazole containing units.

Structure–property relationship can be established by determining the microstructure, which in turn is essential to study the photophysical properties of the copolymer [25–30]. High-resolution 1D and 2D NMR spectroscopy have proved to be one of the most informative and revealing techniques for the investigation of polymer microstructure. Various stereochemical studies on acrylates, methacrylates, methacrylonitrile have been done by Brar et al. [31–35].

* Corresponding author. Tel.: +91 11 26591377.
E-mail address: asbrar@chemistry.iitd.ernet.in (A.S. Brar).

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In this article, the detailed microstructure of 9-ethyl-3-hydroxymethylcarbazolyl acrylate/methacrylonitrile (C/N) copolymers using 1D (^{1}H, ^{13}C{^{1}H}, DEPT) and 2D (HSQC, TOCSY, HMBC) NMR techniques has been reported [36–39]. 2D HMBC studies further assists by providing long-range carbon/proton couplings.

2. Experimental

2.1. Materials

9-Ethyl-3-hydroxymethylcarbazolyl acrylate (C) was prepared as reported in earlier paper [40,41], Methyl methacrylonitrile (N, Merck, 98%) was dried over CaH_2, vacuum distilled and kept below 5 °C. 2,2′-Azobisisobutyronitrile (AIBN, Fluka) was recrystallized using methanol and stored at low temperature.

2.2. Polymerization

Synthesis of poly(9-ethyl-3-hydroxymethylcarbazolyl acrylate-co-methacrylonitrile) was carried out by solution polymerization using benzoyl peroxide (0.05%) as initiator at 60 °C in distilled toluene as solvent. C/N copolymers with different molar infeed ratios were synthesized (Table 1). Filtration of the obtained copolymer was carried out which was further purified by dissolving in minimum amount of chloroform and reprecipitating in methanol.

2.3. Characterization

Various 1D (^{1}H, ^{13}C{^{1}H}, DEPT) and 2D (HSQC, TOCSY, HMBC) NMR experiments for different copolymer composition were recorded on Bruker DPX-300 spectrometer in $CDCl_3$. The ^{1}H and ^{13}C{^{1}H} NMR measurements were made at frequencies of 300.13 and 75.5 MHz, respectively, at 25 °C with standard pulse sequence, as reported in our earlier publications [42,43]. Measurements were done on 10% (w/v) polymer solution. ^{1}H NMR spectra were used to calculate the copolymer composition.

The weight average molecular weight (M_w) and poly dispersity index (PDI, M_w/M_n) were measured using gel-permeation chromatography (GPC) system equipped with

Table 1
Theoretical and experimental F_C, % conversion, molecular weight distribution and T_g of C/N copolymers

Infeed molar fraction (f_C)	Conversion (wt%)	Outfeed molar fraction (F_C)		Molecular weight distribution $M_W \times 10^{-3}$ (g/mol)	Poly dispersity index (PDI)	T_g (°C)
		Experimental	Theoretical			
1.0	–	–	–	8.0	1.60	128
0.8	3.8	0.73	0.72	1.53	1.71	95
0.5	3.0	0.45	0.46	3.68	1.52	86
0.2	2.4	0.19	0.20	5.34	1.56	67

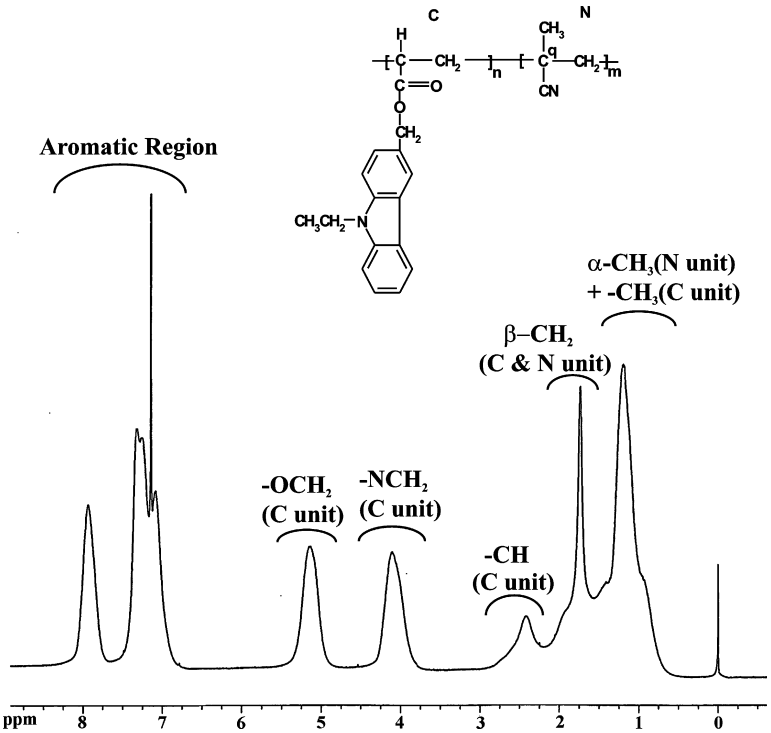

Fig. 1. ^{1}H NMR spectrum of C/N copolymer for $F_C = 0.45$ in $CDCl_3$ at 25 °C.