Thermal characterization of novel *p*-nitrobenzylacrylate–diisopropyl fumarate copolymer synthesized under microwave energy

Tamara G. Oberti · José Luis Alessandrini · M. Susana Cortizo

Abstract Copolymers of *p*-nitrobenzyl acrylate and diisopropyl fumarate with different feed ratios were synthesized under microwave and thermal heating conditions, and then characterized by IR, ^{1}H-, and ^{13}C-NMR spectroscopy. Average molecular weights were analyzed by size exclusion chromatography (SEC). Monomer reactivity ratios were obtained from an extended Kelen–Tüdös method. Differential scanning calorimetry and thermogravimetry were used to evaluate the thermal behavior of all copolymers synthesized under microwave energy. Based on the products analyzed by SEC and gas chromatography–mass spectrometry, a possible mechanism of degradation is postulated.

Keywords *p*-nitrobenzyl acrylate · Glass transition temperature · Microwave polymerization · Thermogravimetry analysis · Thermal degradation

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Introduction

Research on polymers thermal degradation results quite relevant not only for a number of applications that depend on their thermal stability, service life, and recycling processes, but also for the understanding of their structure–property relationship. Homo- and copolymers derived from acrylic and methacrylic esters are the materials most used in various industries because of their chemical, rheological, mechanical, electrical, and optical properties [1–4] among others. Indeed, these properties make them suitable for numerous applications in different fields of science as well as industry.

The thermal behavior of some polyalkylacrylates, polyalkylmethacrylates, and related copolymers has been extensively studied [5–8]. Despite their close structural similarity, the degradation behavior of polyacrylates is significantly different from that of polymethacrylates [9]. Crosslinking, polymer yellowing, high formation of oligomeric species, and evolution of alcohol and carbon dioxide are characteristics of the breakdown of many polyacrylate esters, but not of the corresponding methacrylate polymers.

Few studies on the thermal degradation of polyacrylates and polymethacrylates including aromatic substituents [10–14] have developed a systematic analysis of the effect of the monomer structure on thermal behavior. Gargallo et al. [15] studied a series of poly(dialkylphenyl) methacrylates and analyzed the effect of aromatic substitution on the thermal stability of these polymers. Functionalized by aromatic substituents, polyacrylates result quite useful for the synthesis of polypeptides, antimicrobial agents, scavenger free chlorine atoms, and other optic-related applications [12, 16–18].

The homopolymerization behavior of *p*-nitrobenzyl acrylate (NBA) [18] and diisopropyl fumarate (DIPF) [19]

initiated by benzoyl peroxide under microwave energy has been systematically studied. In both cases, a significant enhancement of the reaction rate with respect to the thermal conditions was observed. The most outstanding difference found was the prevalence of the chain transfer reaction over the chain propagation reaction in the case of NBA, which precludes macroradical growth. Since this type of reaction was absent during DIFP macroradical propagation, high average molecular weight was observed. Radical copolymerization between DIPF and benzyl acrylate (BA) induced by the use of specifically designed equipment for microwave synthesis, showed significant differences when compared with reactions started under thermal conditions [20]. Monomer reactivity ratios r_1 and r_2 were twofold higher under microwave conditions than under thermal conditions, which show that the radical reactivity varies according to the heating mode. These findings encouraged the study of the copolymerization behavior of NBA and DIPF monomers under microwave conditions as well as the effect of composition on their properties, in view of future applications.

The objective of this work was to study the thermal behavior of copolymers from NBA and DIPF obtained by radical copolymerization under microwave irradiation as alternative energy source. The reaction was also tested under thermal heating conditions in order to compare both heating methods. Materials were characterized by spectroscopic techniques and size exclusion chromatography (SEC), while reactivity ratios were determined using the Kelen–Tüdös method.

Experimental

Materials and instruments

Diisopropyl fumarate and NBA monomers were prepared and purified as previously described [18, 19]. Benzoyl peroxide (BP) was recrystallized from methanol. Other reagents used were purchased from Merck and Sintorgan (PA).

A Shimadzu IR-435 spectrometer was used to record the infrared spectra of poly(p-nitrobenzyl acrylate-co-diisopropyl fumarate), poly(NBA-co-DIPF), as a capillary film onto a sodium chloride (NaCl) window.

^{1}H-NMR spectra of polymers were recorded with a Variam-200 MHz (Mercury 200) at 35 °C in CDCl$_3$.

The molecular weight distribution and average molecular weights were determined by SEC with a LKB-2249 instrument at 25 °C and a UV–Visible detector (SPD-10A Shimadzu). A series of four μ-Styragel columns (10^5, 10^4, 10^3, and 100 Å pore size) were used with chloroform as eluent. The sample concentration was 4–5 mg mL^{-1} and

the flow rate was 0.5 mL min^{-1}. Polystyrene standards supplied by Polymer Laboratories and Polysciences Inc. were used for calibration.

A microwave oven (Zenith, ZVP-2819) of 2450 MHz microwave frequency and 700 W maximum power was used for the polymerization reaction.

Glass transition temperatures (T_g) were measured using a differential scanning calorimeter (Shimadzu-TA60). Samples (~ 5 mg) were weighed and scanned at 10 °C min^{-1} from 30 to 150 °C under dry nitrogen (30 mL min^{-1}). Three consecutive scans were performed for each sample: heating/cooling/heating. The value listed is the average for several measurements conducted for each composition.

Thermogravimetry (TG) analysis was performed in a TGA-51 Shimadzu thermogravimetric analyzer. The temperature range was 25–700 °C, at 10 °C min^{-1} heating rate, 40 mL min^{-1} nitrogen flux, and 2–7 mg mass sample.

Gas chromatography–mass spectrometry (GC–MS) of the degraded sample was carried out with a HP 5890 Chromatograph coupled to a HP 5972 A mass selective detector (interface temperature = 300 °C). A HP5-MS capillary column (30 m × 0.25 mm × 5 μm) was used. The linear velocity of helium as carrier gas was 0.6 mL min^{-1}. Electron ionization was maintained at 70 eV.

Copolymerization

Radical copolymerization was carried out in bulk, initiated by BP under microwave energy, following the methodology previously reported [19]. Different amounts of both monomers together with the previously weighed mass of the initiator (40 mM) were charged into each reaction vessel and then purged with N$_2$ during 30 min. Reaction vessels were irradiated at 70 W during 15 min; under these conditions, temperature reached 76 °C. After kept at room temperature, the polymer was isolated by methanol addition, purified by solubilization–precipitation (chloroform:methanol, 1:5), and then dried at constant weight for conversion (C%) estimation. Temperature of the sample was measured with an accurate mercury thermometer at the end of the reaction and recorded in less than 10 s, following the technique previously published [19].

To compare the method previously described, we carried out a thermal copolymerization at 76 °C using a thermal bath during 1,440 min and the same initiator concentration (40 mM).

Thermal degradation

Sixty milligrams of a representative sample of poly(NBA-co-DIPF) were poured into a glass round-bottom flask connected to a jacketed condenser and gas trap in

atmospheric air. For the thermal degradation of the sample, the flask was placed into a heating mantle at 300 °C (temperature selected according to the TG thermogram). After this, the final products were dissolved in chloroform and analyzed by SEC. This fraction was filtered by means of a silica column, using chloroform as eluent to isolate low molecular weight components. Later, this last fraction was analyzed by GC–MS.
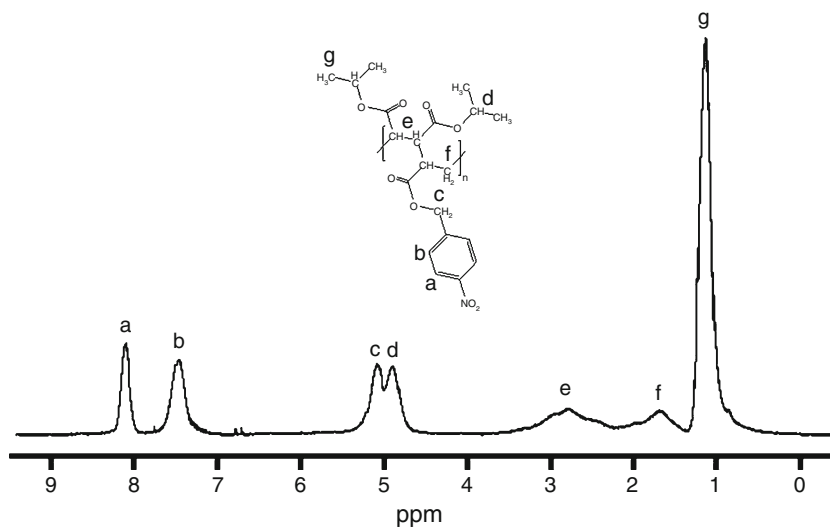
Results and discussion

Copolymer synthesis and characterization

Previous studies on DIPF and NBA homopolymerizations under microwave energy have demonstrated a significant enhancement of the reaction rate in comparison with thermal polymerization conditions [18, 19]. In this study, copolymers from monomers with different relative content were synthesized under microwave energy. Scheme 1 shows the structure of poly(NBA-co-DIPF), confirmed by spectroscopic methods. IR (thin film): (cm^{-1}), 3120, 3081 (C–H Ar), 2984, 2930, 2876 (C–H alif), 1736 (C=O), 1609 (C=C Ar), 1522, 1346 (NO$_2$), 1260 and 1106 (CO-OR), 853 (C-NO$_2$). ^{1}H-NMR peaks were assigned according to
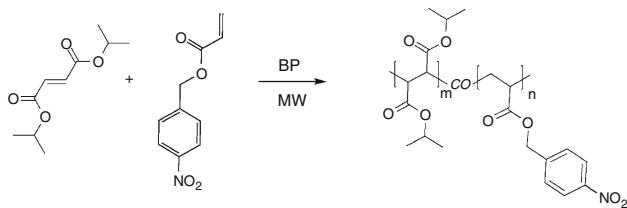
the corresponding homopolymers spectra. Figure 1 shows a characteristic spectrum. ^{1}H-NMR (CDCl$_3$): δ(ppm), 1.17 (–CH$_3$), 1.68 (–CH$_2$–), 2.81 (–CH<), 4.90 (–O–CH<), 5.12 (–OCH$_2$–Ar), 7.52–8.14 (H–Ar).

Composition was estimated from the integral ratio of the peaks at 8.14 and 1.17 ppm corresponding to aromatic *meta*-hydrogen (Ar) of NBA and methyl hydrogen (CH$_3$) of DIPF, respectively, using the following ratio:

$$F_1 = 6I(\text{Ar})/\left[6I(\text{Ar}) + I(\text{CH}_3)\right] \tag{1}$$

where F_1 is the mole fraction of NBA in the copolymer and $I(\text{Ar})$ and $I(\text{CH}_3)$ represent the ^{1}H-NMR resonance peak areas at 8.14 and 1.17 ppm, respectively. Table 1 summarizes the feed (f_1), copolymer (F_1) compositions, and properties of the copolymers obtained. The reaction conversion of the copolymers was always higher than that of homopolymers. On the other hand, copolymerization under microwave conditions showed a significant acceleration of the reaction rate: 1.07 and 0.018% conversion/min for microwave and thermal conditions respectively ($f_1 = 0.13$), under similar experimental conditions. The average molecular weight (M_w) increased when F_1 decreased, which suggests low reactivity of the NBA monomer, as previously reported [18]. Similar results were observed under thermal conditions.

Monomer reactivity ratios determination

The determination of reactivity ratios of monomer pairs allows understanding the copolymerization behavior of monomers. The plot of NBA mole fractions in the feed versus that in the copolymer is shown in Fig. 2. It clearly illustrates that NBA composition in the copolymer is always higher than that in the feed. This behavior was observed in both microwave and thermal polymerizations. In order to determine the copolymerization behavior at

Scheme 1 Copolymerization reaction

Fig. 1 ^{1}H-NMR spectrum of poly(NBA-co-DIPF) with $F_1 = 0.66$ obtained under microwave energy

Table 1 Copolymerization of NBA with DIPF, [BP] = 40 mM

Conditions	f_1*	F_1*	C/%	$M_w \times 10^{-3}$/g mol^{-1}	M_w/M_n
MW	0.00	0.00	2.8	273.6	6.60
	0.13	0.27	16.0	22.9	2.10
	0.25	0.44	26.6	13.7	1.80
	0.40	0.66	32.7	10.3	1.72
	0.70	0.84	21.7	3.1	1.48
	1.00	1.00	10.5	1.9	1.30
Thermal	0.13	0.18	26.3	555.5	13.32
	0.25	0.44	39.6	56.8	2.60
	0.50	0.64	66.1	32.8	2.20
	0.87	0.95	56.5	2.3	1.51

Microwave conditions (MW): P = 70 W, 15 min (76 °C); thermal conditions: 76 °C, 1440 min

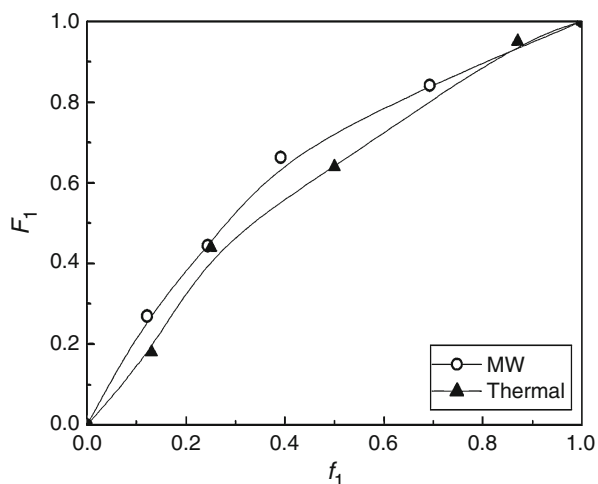* f_1 and F_1 are the mole fraction of NBA in the feed and in the copolymer, respectively

Fig. 2 Copolymer composition plot for the NBA–DIPF system. [BP] = 40 mM. Microwave conditions (MW): P = 70 W, 15 min (76 °C); thermal conditions: 76 °C; 1,440 min

high conversion polymerization, the reactivity ratio was calculated by the conversion methods modified by Kelen and Tüdös [21, 22]. Monomer reactivity ratios r_1 and r_2 (NBA and DIPF, respectively) were determined (Table 2) by applying this methodology to the comonomer–copolymer composition curve (Fig. 2). Values obtained with $r_1 \gg r_2$ showed low reactivity of DIPF to NBA, an electron-accepting monomer as observed in other comparable systems [23]. Similar behavior was found in the radical copolymerization of DIPF with BA under microwave conditions [20]. The product $r_1 r_2 = 1.38$ with $r_1 \gg 1$ and $r_2 < 1$ indicates that both propagating macroradicals have a preference for the addition of NBA monomer but with a random distribution of the monomeric units. On the other

hand, the relative reactivity of both acrylate monomers (NBA and BA) with DIPF can be determined from the inverse of the monomer reactivity ratio (1/r). In this study, reactivity values of NBA and BA monomers to the fumarate radical were 3.24 and 16, respectively (see Table 2), indicating highest reactivity for BA.

Thermal properties

The physical response of homo- and copolymers against thermal stress results quite relevant in view of future applications. Therefore, glass transition temperature and thermal stability of synthesized copolymers were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TG). Table 3 shows the results obtained. DSC study demonstrated that all copolymers present a single T_g and that values mainly depend on the composition of the comonomers, increasing when the mole fraction of NBA in the copolymer decreases. This behavior can be explained by comparison of the monomer chemical structure (Scheme 1), since DIPF, a 1,2-disubstituted ethylenic monomer, presents a more rigid chain than acrylic monomer [24].

The thermal stability of copolymers was assessed by TG under nitrogen atmosphere; their decomposition curves are depicted in Fig. 3. All copolymers seemed to decompose in a two-stage process and showed higher initial decomposition temperatures (IDT) than the corresponding homopolymers (Table 3), indicating higher thermal stability. Other acrylic ester copolymers derived from aromatic alcohols showed similar thermal behavior, with IDT values between 250 and 300 °C [25]. Polydiisopropyl fumarate (PDIPF) degraded in a single step starting at 250 °C, according to previously reported data [26]. Degradation activation energies (E) of the sample were calculated from non-isothermal TG curves using the Freeman and Carroll equation [27], assuming a first order reaction kinetics. Although the maximum rate of degradation (T_{max1}) is similar for all polymers (320–330 °C), degradation activation energies (E) were different. As shown in Fig. 3 and Table 3, poly-p-nitrobenzyl acrylate (PNBA) which presents the lowest E value, decomposes more easily than the other polymers. PNBA degraded in a two-step process, the first of which represents the lowest mass loss (14.7%), while for copolymers, the greatest mass loss was observed during the first stage of decomposition. The first mass loss observed for PNBA could correspond to the loss of decomposition products of low molar mass, as will be shown later, while the highest mass loss during the second stage of decomposition could correspond to the scission of the main chain.

On the other hand, an increase in thermal stability of copolymers was observed when NBA content increased up

Table 2 Values of reactivity ratios r_1 and r_2 and the product $r_1 r_2$ for radical copolymerization of benzyl acrylate monomers (M_1) with DIPF (M_2)

M_1	Conditions	r_1	r_2	$1/r_2$	$r_1 r_2$	Reference
NBA	MW	4.459	0.309	3.24	1.38	This study
NBA	Thermal	3.842	0.565	1.77	2.17	This study
BA	MW	2.456	0.062	16	0.15	[20]

Table 3 DSC and TG data of homo and copolymers of NBA obtained under microwave energy
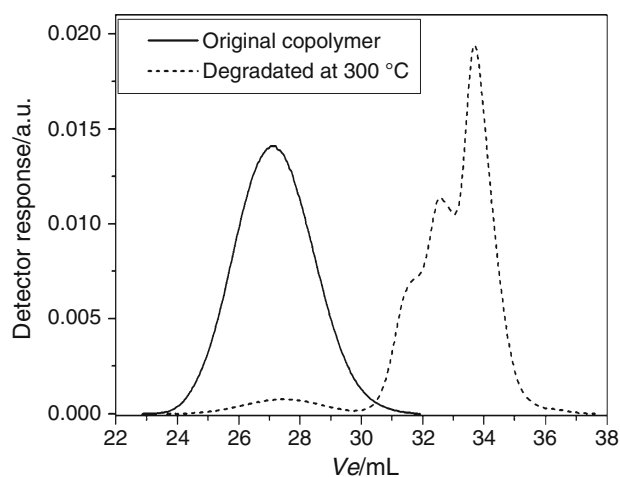
F_1	$T_g/°C$	IDT	T_{max1}	T_{max2}	E/kJ mol^{-1}	r^2
0.00	75.0	250	318(53.9)	–	228.6	0.94
0.27	64.1	280	332(51.3)	616(95)	226.8	0.97
0.44	57.9	272	332(46.5)	490(88.5)	254.6	0.99
0.66	51.5	290	331(35.9)	452(90.3)	362.0	0.95
0.84	47.8	290	327(41.7)	475(81.9)	189.6	0.97
1.00	42.0	220	320(14.7)	580(67.3)	142.3	0.94

Value in parentheses indicates the total mass loss (%) up to the stated temperature
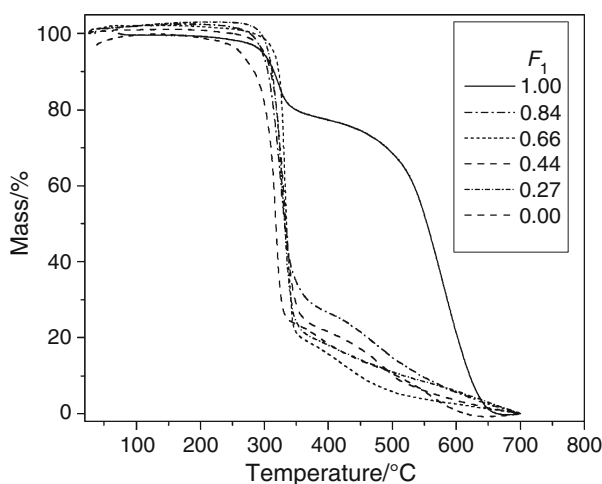
Fig. 3 TG curves of poly(NBA-*co*-DIPF) under nitrogen atmosphere at heating rate of 10 °C min^{-1}. F_1 is the mole fraction of NBA in the copolymer

Fig. 4 Chromatographic profile of original copolymer ($F_1 = 0.66$) and degraded copolymer at 300 °C

to 0.66. It was not possible to establish an order of stability based only on the composition copolymer, probably due to different average molecular weights of samples. In fact, the last two polymers exhibited a M_w one order of magnitude lower than M_w of the other polymers.

PDIPF degradation mechanism studied by pyrolysis gas chromatography demonstrated that the main degradation products were isopropyl alcohol and DIPF monomer, with a ratio (alcohol/monomer) of 32.0 at 400 °C under nitrogen atmosphere [26]. On the other hand, the corresponding mechanism for *p*-nitrophenyl acrylate–styrene copolymers has been suggested to occur along four stages [28], with loss of CO_2, benzene ring, NO_2 and the final complete loss of the polymer backbone. For this study, it is possible that a

combination of both processes might have occurred. In order to go further into the chemical mechanism of degradation, we carried out a simple degradation test at 300 °C. Figure 4 shows the chromatographic profile of original and degraded copolymers. The elugram from degraded copolymers displays a bimodal distribution which exhibited a small fraction of the undegraded copolymer and another one corresponding to the degradation products at high elution volumes (low molecular weight). The main fraction was split into at least three subfractions. Degradation products were separated through a chromatographic column and then analyzed by GC–MS. The gas chromatogram of this last fraction, illustrated in Fig. 5, presented three peaks at 3.58, 4.58, and 5.04 min. The analysis of the mass spectra (not shown) of each component
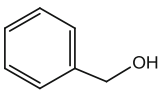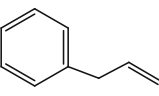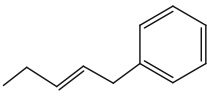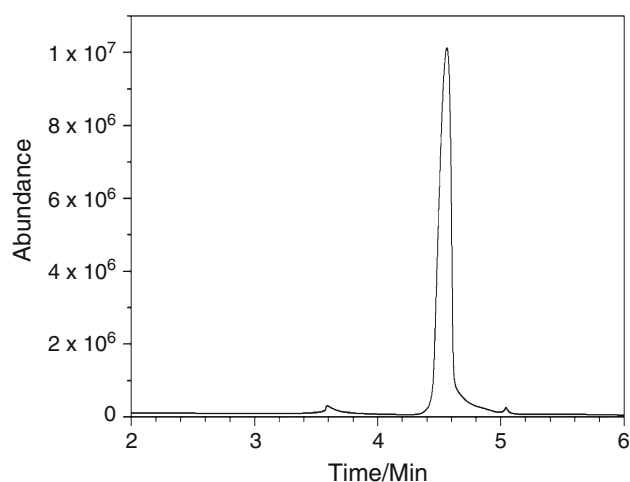
Fig. 5 Gas chromatogram of degradation products from low molecular weight fraction

Table 4 Identification by GC–MS of the degradation products from low molecular weight fraction of poly(NBA-*co*-DIPF)

Retention time/min	Assignment	*m/z* of major peaks and structures	
3.58	Benzyl Alcohol $M^+ = 108$	91	$C_6H_5-CH_2^+$
		79	$C_5H_3O^+$
		77	$C_6H_5^+$
		51	$HC\equiv C-CH=CH^+$
4.58	Allylbenzene $M^+ = 118$	117	$C_6H_5-CH_2-CH=CH^+$
		90	$C_6H_4-CH_2^+$
		77	$C_6H_5^+$
		39	$CH\equiv C-CH_2^+$
5.04	1-Phenyl-2-pentene $M^+ = 146$	117	$C_6H_5-CH_2-CH=CH^+$
		104	$C_6H_5-CH_2-CH^+$
		91	$C_6H_5-CH_2^+$
		77	$C_6H_5^+$
		51	$HC\equiv C-CH=CH^+$
		39	$CH\equiv C-CH_2^+$

allowed us identify the structure (Table 4). The presence of benzyl alcohol, NO_2 (by phenomenological observation) suggests a cleavage reaction of the pendent group while that in the other products (allylbenzene and 1-phenyl-2-pentene) could be due to radical rearrangements in main chain. Iqbal et al. [29] studied the thermal behavior of glycidyl methacrylate–acrylonitrile copolymers, demonstrating that the degradation mechanism takes through the

formation of radicals in the main chain pendant acrylonitrile groups, with loss of small fragments containing these acrylonitrile units. Based on the above facts, a radical degradation mechanism was proposed (see scheme 2 and scheme 3 in Supporting Information), in accordance with that previously reported for similar compounds [5, 26]. The initial step suggested is the formation of the relatively stable radical aromatic from the $C-NO_2$ bond cleavage and the initiation of all major composition products by this radical.

Conclusions

Copolymers from NBA and DIPF under microwave and conventional thermal heating conditions were synthesized and characterized. Greater effectiveness of the reaction under microwave conditions was evidenced by the high increase in the reaction conversion. Reactivity ratios determined under both reaction conditions showed similar behavior for both propagating macroradicals, with some preference for NBA monomer addition but with a random distribution of the monomeric units along the polymeric chain.

An increase in T_g value of the copolymers was observed when the mole fraction of NBA in the copolymer decreased due to the inherent stiffness of DIPF comonomer. The analysis of TG curves demonstrated that all copolymers show a two-step thermal degradation profile and higher thermal stability up to 270–290 °C than the corresponding homopolymers. The mechanism of poly(NBA-*co*-DIPF) thermal degradation suggested includes pendent group and main chain scission initiated from the stable radical aromatic.

Both the synthesis method and the thermal stability of these copolymers make them potentially suitable for various applications in high temperature conditions, such as heat resistant and ablative materials.

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