

*Dedicated to the memory of
Professor Maria Brezeanu (1924–2005)*

ALTERNATING COPOLYMERS FROM N-(4-FORMYLPHENOXY-4'-CARBONYLPHENYL)MALEIMIDE. A COMPARATIVE STUDY

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The synthesis of a maleimide with an aldehyde pendant group, N-(4-formylphenoxy-4'-carbonylphenyl)maleimide (FCPMI), was described. Two copolymers were obtained by the copolymerization of N-(4-formylphenoxy-4'-carbonylphenyl)maleimide with styrene (St) (copolymer **I**) and N-vinyl-2-pyrrolidone (NVP), respectively (copolymer **II**). The copolymerizations were performed under various conditions and led to alternant copolymers. The structural characterization was achieved by IR and ¹H-NMR spectroscopy, gel permeation chromatography (GPC), elemental analysis, differential scanning calorimetry (DSC) and dynamic thermo-gravimetry. The monomers reactivity ratios were calculated by extended Kelen-Tüdös and Mao-Huglin methods. The average reactivity ratios were found to be $r_1=0.046$, $r_2=0.008$ for FCPMI / St system and $r_1=0.044$, $r_2=0.060$ for FCPMI / NVP system. The monomer sequences distribution along the copolymer chains was also discussed. The initial decomposition temperatures and the glass transition temperatures increased with the increasing mole fraction of N-aryl maleimide in the copolymers. N-(4-formylphenoxy-4'-carbonylphenyl)maleimide and its corresponding copolymer with styrene exhibited liquid crystalline behavior.

INTRODUCTION

Purposeful development of polymeric materials combining high thermal and mechanical performances with specific functional properties is a new direction in polymer synthesis, due to the increasing need in the high-technology industries. Maleimide type polymers appear very interesting from this point of view.

N-substituted maleimides (RMI) are important reagents to improve the thermal behavior of common vinyl polymers and resins.^{1,2} One outstanding property of RMIs is their susceptibility to a variety of chemical reactions as a result of the electron withdrawing effect of the two adjacent carbonyl groups in maleimide ring, which create a very electron-deficient double bond. Maleimide polymers have a good stability with high transition temperatures due to the polar five-membered imide ring structure.

There are many reports on homo- and copolymerization of maleimide monomers.^{3,4} The copolymerization involving N-substituted maleimides gave the possibility to prepare new materials with improved properties such as flame and heat-resistance, thermal and chemical stability.⁵⁻⁷ The synthesis of thermally stable and photosensitive functional copolymers based on N-substituted maleimides or different types of maleimide/vinyl ether UV-curable systems have been reported.⁸⁻¹⁰ These polymers are very useful in microelectronics as thermally stable photoresists in lithography or image-marking processes.^{11,12} Other maleimide-incorporated vinyl polymers have been reported for their optical and catalytic activities^{13,14} or for the ability to function as ion-exchangers or photoinitiators.^{15,16} Interesting properties recommend some of them as non-linear-optical materials (NLO),¹⁷ Langmuir-Blodgett films¹⁸ or for specific applications based on their low dielectric constant or their ability to induce asymmetric polymerization processes.^{19,20}

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This paper presents a comparative study concerning the copolymerization of *N*-(4-formylphenoxy-4'-carbonylphenyl)maleimide (FCPMI), as acceptor monomer with two donor monomers, styrene (St) and *N*-vinyl-2-pyrrolidone (NVP), using the radical initiation.

RESULTS AND DISCUSSION

Structural characterization

The peculiar homo- and copolymerization characteristics of the electron-deficient maleimide group make it an attractive monomer for designing special vinyl polymers. This 1,2-ethylene disubstituted type structure is a five-membered planar ring which completely hinders the imide residues rotation around the chain of the molecule; that determines a great structural stiffness and a high thermal stability of the resulting copolymers. At the same time, the reactive pendant group serves to directly modify the polymer properties or to participate in addition, grafting and others chemical modification reactions.

The radical copolymerizations of FCPMI (monomer 1) with vinyl monomers, St or NVP, (monomer 2), were performed in two aprotic dipolar solvents, dimethylsulfoxide (DMSO) and dimethylformamide (DMF), at two different temperatures (60°C, 90°C), using 2,2'-azobisisobutyronitrile (AIBN) as initiator. The chemical structures of the monomer and the resulting copolymers are presented in Fig. 1.

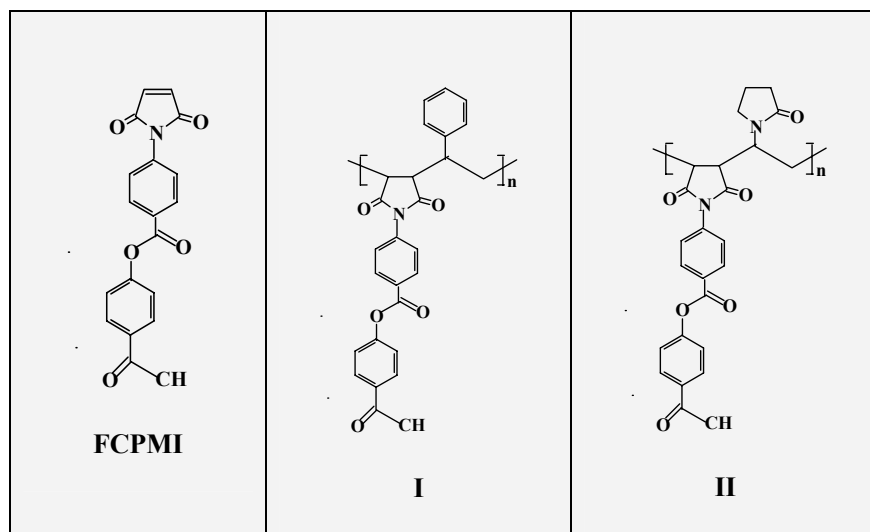


Fig. 1 – Chemical structures of: *N*-(4-formylphenoxy-4'-carbonylphenyl)maleimide (FCPMI), poly[*N*-(4-formylphenoxy-4'-carbonylphenyl)maleimide-*co*-styrene] (I), poly[*N*-(4-formylphenoxy-4'-carbonylphenyl)maleimide-*co*-*N*-vinyl-2-pyrrolidone] (II).

FCPMI was characterized by elemental analysis, infrared and proton nuclear magnetic resonance spectroscopy.²¹ The optical polarized light microscopy (OPM) measurements confirmed that the monomer exhibit birefringence in melt. The granular textures of the mesophase (Fig. 2), as observed by OPM, are difficult to assign.²²

The copolymerizations of systems FCPMI/St and FCPMI/NVP were studied in a wide composition interval with mole fractions of RMI ranging from 0.10 to 0.90 in the monomer feed. The copolymerization data and some characteristic properties of the resulting copolymers are given in Table 1.

The chemical structure of the synthesized copolymers with styrene were confirmed by elemental analysis, IR and ¹H-NMR spectroscopy.²¹ Fig. 3 shows the ¹H-NMR spectrum of the new resulting copolymer poly(FCPMI-*co*-NVP) (sample 9, Table 1).

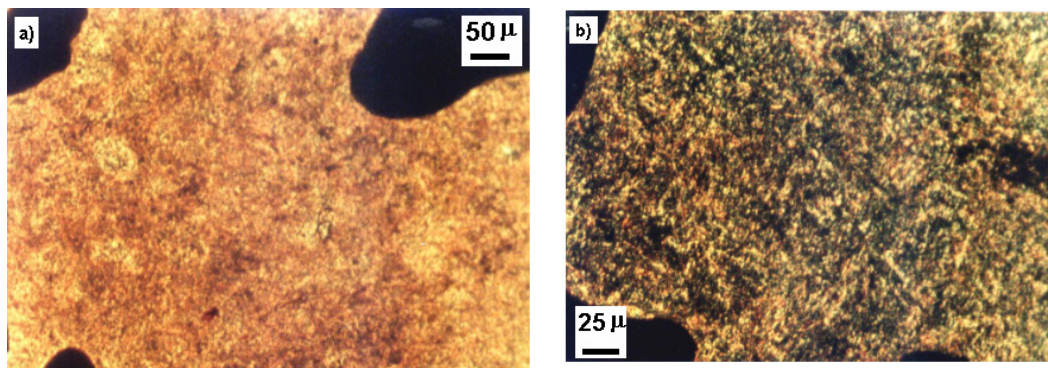


Fig. 2 – OPM microphotographs of N-(4-formylphenoxy-4'-carbonylphenyl)maleimide: a) 227°C, ×200; b) 227°C, ×400.

Table 1

Copolymerization data of N-(4-formylphenoxy-4'-carbonylphenyl)maleimide (M_1) with vinyl monomers (M_2)^{a,b}

Sample	M_1 in feed (mole fraction)	m_1 in copolymer (mole fraction)	conv. %	$R_p \cdot 10^5$ ^c $\text{mol} \cdot \text{l}^{-1} \cdot \text{min}^{-1}$	M_n^d $\cdot 10^{-3}$	M_w/M_n	IDT ^e (°C)	T_m^f (°C)	T_g^f (°C)
N-(4-formylphenoxy-4'-carbonylphenyl)maleimide - Styrene (I) ^a									
1	0.10	0.4300	54.23	2.851	6.3	1.27	292	-	-
2	0.20	0.5000	35.50	1.596	6.7	1.19	305	-	-
3	0.28	0.4900	29.91	1.196	5.3	1.20	307	-	-
4	0.30	0.5000	28.50	1.112	4.8	1.25	310	216	106
5	0.50	0.5100	22.66	0.704	3.3	1.90	307	228	108
6	0.70	0.5300	25.77	0.664	3.2	1.25	328	220	112
N-(4-formylphenoxy-4'-carbonylphenyl)maleimide - N-vinyl-2-pyrrolidone - (II) ^b									
7	0.10	0.3500	26.20	4.609	20.30	1.4	230	-	-
8	0.30	0.4720	30.90	4.248	9.20	1.4	246	-	129
9	0.50	0.4900	28.60	3.045	5.10	1.3	250	-	122
10	0.70	0.5260	11.50	1.038	4.10	1.2	255	-	120
11	0.90	0.5970	9.10	0.695	2.50	1.3	262	-	123

^a Solvent: DMSO = 15 ml; $M_1 + M_2 = 1.0$ g; [AIBN] = 0.3 mol%; polymerization time = 7 days; temp. = 60°C;

^b Solvent: DMF = 10 ml; $M_1 + M_2 = 1.0$ g; [AIBN] = 0.3 mol%; polymerization time = 3 days; temp. = 90°C;

^c Rate of polymerization;

^d Determined by GPC;

^e Initial decomposition temperature (onset on the TGA curve);

^f T_m – melting temperature and T_g – glass transition temperature from DSC.

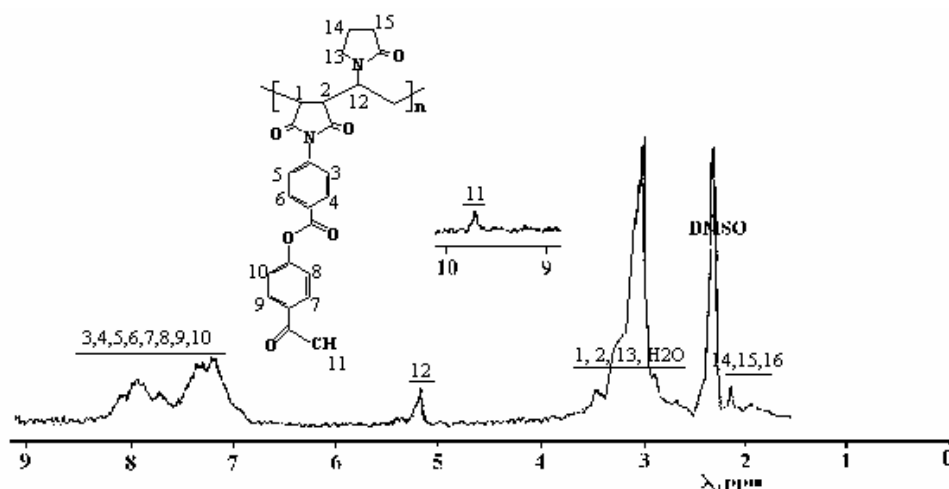


Fig. 3 – ¹H-NMR spectrum of the copolymer **II** (sample 9) in DMSO- d_6 at room temperature.

One can see at about 9.70 ppm, in offset, the signal attributable to the aldehyde proton resonance. The aromatic proton appears as a multiplet absorption between 8.20-7.15 ppm, while the methine proton resonance of NVP appears as a singlet at 5.23 ppm. The peaks in the range of 3.20-3.40 ppm, assigned to the methine protons of the imide ring and the methylene protons of NVP in the side chain ($^{13}\text{CH}_2$), respectively, are overlapped by the water resonance protons signal. Other methylene protons can be detected between 2.00-2.25 ppm ($^{14}\text{CH}_2$, $^{15}\text{CH}_2$, $^{16}\text{CH}_2$).

The investigations by DSC and OPM revealed a liquid crystalline behavior, under mechanical stress, for the copolymer **I**. OPM measurements at 242°C showed the appearance of a strong birefringence (Fig. 4b) when the superior lamella was mechanically pressed. At the removal of this force, the birefringence disappears. The copolymer **II** did not exhibit any birefringence in the melt.

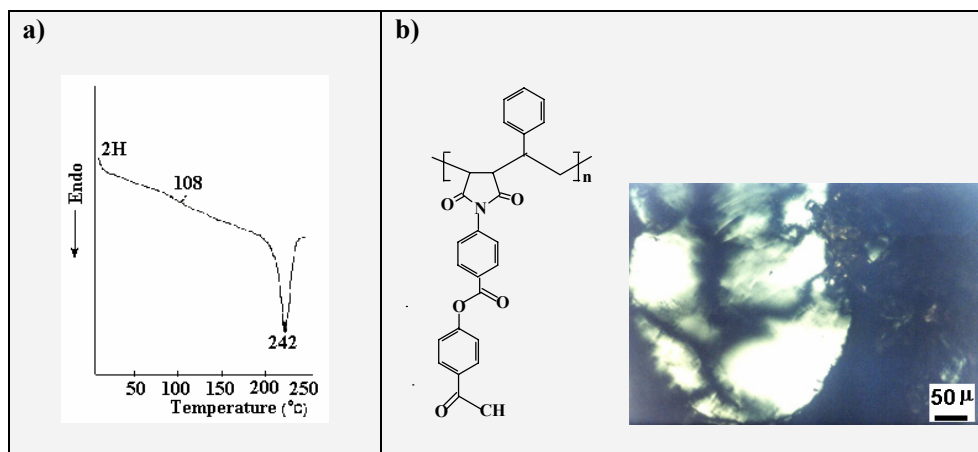


Fig. 4 – a) DSC thermograms of copolymer **I** (sample 5), 2H – second heating cycle at 10°C/min; b) OPM microphotograph of copolymer **I** (sample 5), 248°C, $\times 200$, under mechanical stress.

The resulting polymers are soluble in aprotic dipolar solvents such as: *N*-methylpyrrolidone, dimethylformamide, dimethylsulfoxide and tetrahydrofuran. Their good solubility is due both the flexible linkages in the main chain and the pendant groups which reduce the tight packing of the macromolecules. The disturbed packing facilitates the diffusion of small molecules of solvents and, by way of consequence, leads to a better solubility.

Copolymer composition

It is known that the copolymerization of *N*-phenylmaleimide with styrene yields a “nearly equimolecular” alternating copolymer, irrespective of the monomer feed, while the reaction with vinyl acetate and methyl methacrylate proceeds in the form of statistical copolymerization.¹⁰ If the copolymerization of *N*-phenylmaleimide with styrene gives an exact alternating copolymer for different monomers ratios in the feed, in the copolymerization of *N*-(*p*-carboxyphenyl)maleimide with styrene the alternating character decreases, the phenomenon being also observed in the copolymerization of *N*-(carboxymethyl)maleimide with styrene.²³

Fig. 5 presents the copolymerization diagrams of copolymers **I** and **II**, respectively. Both curves suggest copolymerizations with tendency toward alternation.

The tendency toward an alternating structure is ascribed to the well known system derived from the electron deficient maleimide and the electron rich styrene or *N*-vinyl-2-pyrrolidone monomers.²⁴

Fig. 6 present the effects of the maleimide concentration in the monomer feed on the conversion and the number average molecular weight (M_n), respectively, of the resulting copolymers.

It can be observed that when the concentration of the maleimide monomer feed increases, the conversion of copolymers decreases. At the same time, the M_n value of the copolymers decreases. Two factors, that affect the polymerization in solution, could be the explanation for this phenomenon. One is the rate of diffusion, if the termination is diffusion-controlled, and the other one is the chain transfer to solvent. The presence of a relatively weak tertiary hydrogen atom in the maleimide ring, points towards the second factor. In conclusion it can be assumed that the degradative chain transfer from maleimide radicals cause the decrease of the molecular weight (Fig. 6b). This effect diminishes gradually by increasing the vinyl content in the medium.²⁵

Fig. 5 – Monomer-copolymer composition curves for the copolymerization of FCPMI with St (●) and NVP (▲).

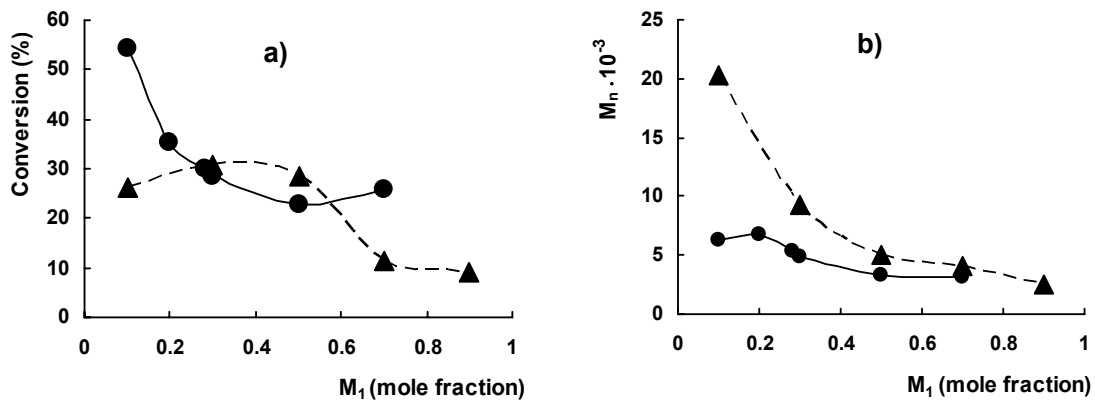
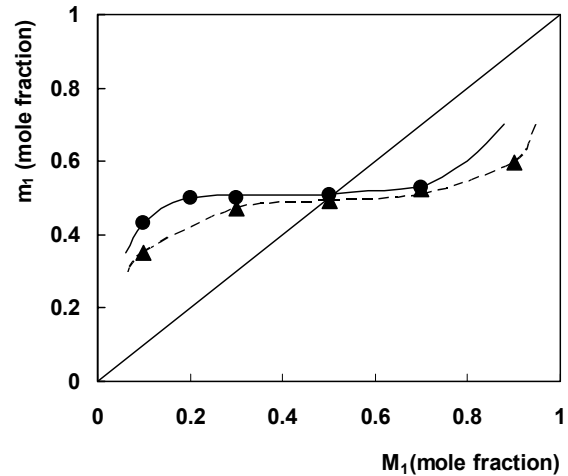


Fig. 6 – Effects of FCPMI concentration in the monomer feed on the conversion (a) and the number average molecular weight (b); (●) for copolymer I and (▲) for copolymer II.

On the other hand, by decreasing the molar ratio of vinyl monomers, the reaction tends to follow a constant rate (Fig. 7) (below: 50 mol% FCPMI in feed for the copolymer I and 30 mol% FCPMI in feed for copolymer II). The linearity of the polymerization rate (R_p) suggests a negligible influence of the structural units on the copolymerization mechanism.²⁵

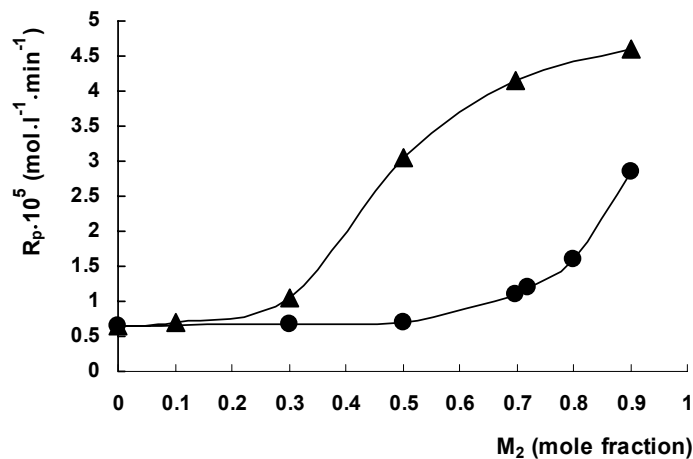


Fig. 7 – Variation of the polymerization rate with the vinyl monomer concentration in the feed for: copolymer I (●) and copolymer II (▲).

Reactivity ratios

The reactivity ratios of the monomers are the significant parameters in the copolymerization process. A complete description of the complex copolymer structure obtained by radical copolymerization implies the relation between the reactivity ratios values. Two methods (applicable to medium conversion data), the extended Kelen-Tüdös (ext K-T)²⁶ and Mao-Huglin (M-H)²⁷, were used to calculate the reactivity ratios of the functional RMI (monomer 1) and the vinyl monomers (monomer 2). In our systems, the highest value of conversion was 55 % (Table 1).

The extended Kelen-Tüdös method is based on the equation:

$$\eta = r_1 \xi - \frac{r_2}{\alpha} (1 - \xi)$$

where $\eta = G/(\alpha + H)$, $\xi = H/(\alpha + H)$, $\alpha = (H_{\min} H_{\max})^{1/2}$.

The parameters G and H are given by the following equations:

$$G = (f - 1)/z; H = f/z^2; z = \log(1 - \tau_1)/\log(1 - \tau_2)$$

$$\tau_2 = [(\mu^0 + F)/(\mu^0 + f)](w/100); \tau_1 = \tau_2 f / F$$

where: w = the weight percent conversion of total monomers; μ^0 = (molecular weight of monomer 2 / molecular weight of monomer 1).

The Mao-Huglin method is an iterative linear method which uses in each step a K-T plot procedure.²⁸ In applied K-T relations, the initial feed composition, F, is replaced with F^c , calculated by the following equation:

$$F^c = \frac{(f^c - 1) + \sqrt{(1 - f^c) + 4r_1 r_2 f^c}}{2r_1}$$

f^c is calculated from the assumed reactivity ratios by the integrated copolymerization equation. The criterion of iteration convergence is that the recalculated reactivity ratios should become equal to the assumed ones. The obtained reactivity ratios data are given in Table 2.

Table 2

Reactivity ratios calculated for the radical copolymerization of FCPMI with St and NVP

System	Method ^a	r_1	r_2
FCPMI			
FCPMI/St	M-H	0.047 ± 0.036	0.008 ± 0.013
	ext K-T	0.046 ± 0.039	0.008 ± 0.014
	Average:	0.046	0.008
FCPMI/NVP	M-H	0.044 ± 0.024	0.061 ± 0.023
	ext K-T	0.044 ± 0.025	0.060 ± 0.024
	Average:	0.044	0.060

^a ext K-T – extended Kelen-Tüdös method; M-H – Mao-Huglin method.

It is obvious that an electron-withdrawing group such an aldehyde function stabilizes the corresponding maleimidic radical by resonance.

Copolymer microstructure

To compare the sequences distribution in the resulting copolymers chains it is necessary to know the distribution of the dyad monomer sequences (Fig. 8). These were calculated by the Igarashi method²⁹ using the following equations:

$$X = m_1 - \frac{2m_1(1-m_1)}{1 + \sqrt{(2m_1 - 1)^2 + 4r_1 r_2 m_1(1-m_1)}}$$

$$Y = (1 - m_1) \frac{2m_1(1 - m_1)}{1 + \sqrt{(2m_1 - 1)^2 + 4r_1r_2m_1(1 - m_1)}}$$

$$Z = \frac{4m_1(1 - m_1)}{1 + \sqrt{(2m_1 - 1)^2 + 4r_1r_2m_1(1 - m_1)}}$$

where: X, Y, Z are the mole fractions of the RMI-RMI, St-St (or NVP-NVP) and RMI-St (or RMI-NVP) dyads in copolymer;
 m_1 is the mole fraction of maleimide monomer in copolymer;
 r_1, r_2 are the reactivity ratios of the monomers.

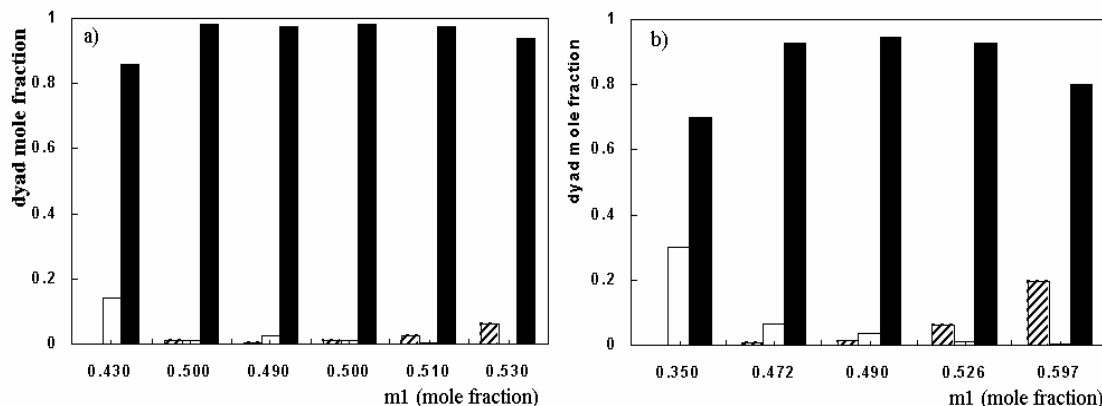


Fig. 8 – Dyad monomer sequence fractions *versus* the mole fraction of maleimide monomer in copolymer **I** (a) and copolymer **II** (b); RMI-RMI dyads – lined columns; St-St (or NVP-NVP) dyads – white columns; RMI-St (or RMI-NVP) dyads – black columns.

One can observe that the alternating sequences degree in both copolymers is very high. As inside every series of polymers, the effect of the copolymer composition implies very small differences on the relation structure–properties (*e.g.*, melting or transition temperatures) we can assume that these features lead to the conclusion that both types of copolymers have a high alternating nature.

CONCLUSIONS

Two rigid maleimide-type copolymers bearing pendant aldehyde group were synthesized *via* radical copolymerization of N-(4-formylphenoxy-4'-carbonylphenyl)maleimide with vinyl monomers (styrene and N-vinyl-2-pyrrolidone). The number average molecular weights of these copolymers are in the range of $2.5 \cdot 10^3$ – $20.3 \cdot 10^3$ and the polydispersities are the range of 1.19–1.90. These polymers exhibit fairly high thermal stability, with decomposition temperatures above 230°C. The very good correlation between the effect of the copolymer composition on the thermal stability, melting temperature and transition temperature demonstrates that the resulting copolymers have a high alternating structure. The investigations by differential scanning calorimetry and optical polarized light microscopy revealed a liquid crystalline behavior for the monomer N-(4-formylphenoxy-4'-carbonylphenyl)maleimide and its copolymer with styrene. The aldehyde group, as a pendant reactive function, may provide valuable supports for coupling reaction with various appropriate reagents.

EXPERIMENTAL

Materials

p-Amino benzoic acid and *p*-hydroxy-benzaldehyde (Fluka) were used without further purification. Maleic anhydride (Aldrich) was sublimed before use. N-vinyl-2-pyrrolidone and styrene, commercial materials from Fluka, were redistilled before use. Solvents such

as: acetone, methanol, dimethylsulfoxide, dimethylformamide, from different commercial sources, were purified by the usual methods.³⁰ 2,2'-Azobisisobutyronitrile was recrystallized from methanol several times (m.p. 103°C).

Monomers and intermediates

N-(4-carboxyphenyl)maleimide (CPMI) was obtained by the reaction between maleic anhydride and *p*-amino-benzoic acid, in dried acetone, at ambient temperature, followed by chemical cyclodehydration.³¹ Yield 82 %, mp: 242-243°C.

Elemental analysis (%): Calculated for C₁₁H₇NO₄ (217): C, 60.83; H, 3.25; N, 6.45. Found: C, 60.48; H, 3.04; N, 5.97. IR (cm⁻¹): 3150, 2980, 2300, 1770, 1700, 1640, 1600, 1390, 1370, 1200, 820, 690. ¹H-NMR (ppm): 13.45-12.78 (s, 1H, COOH), 8.03 (d, 2H, aromatic), 7.49 (d, 2H, aromatic), 7.22 (s, 2H, olefinic).

4-Maleimido-benzoyl chloride was synthesized by the reaction of CPMI with thionyl chloride.³² Yield 78 %, m.p. 166-167°C.

N-(4-formylphenoxy-4'-carbonylphenyl)maleimide (FCPMI) was prepared by a Schotten-Baumann reaction from 4-maleimido-benzoyl chloride and *p*-hydroxy-benzaldehyde presented in detail elsewhere.²¹ Yield 88.6 %, m.p. 222-223°C.

Elemental analysis (%): Calculated for C₁₈H₁₁NO₅ (321): C, 67.28; H, 3.42; N, 4.36. Found: C, 67.71; H, 3.79; N, 3.95. IR (cm⁻¹): 3105, 2870, 2780, 1780, 1720, 1660, 1380, 1150, 695, 935-950. ¹H-NMR (ppm): 9.74-9.62 (s, 1H, aldehyde), 8.06-7.41 (m, 8H, aromatic), 7.12 (s, 2H, olefinic).

Copolymerization procedure

The copolymerizations of the two monomers pairs, FCPMI-St and FCPMI-NVP respectively, were carried out in an aprotic dipolar solvent (DMF, DMSO), in sealed glass tubes under inert atmosphere, using 2,2'-azobisisobutyronitrile as radical initiator (0.3 mol%). The resulting copolymers, poly(N-(4-formylphenoxy-4'-carbonylphenyl)maleimide-*co*-styrene) and poly(N-(4-carboxyphenyl)maleimide-*co*-N-vinyl-2-pyrrolidone) were isolated by precipitation in methanol and dried under vacuum at room temperature.

Measurements

The IR spectra were recorded on a Specord M 90 Carl Zeiss Jena Spectrophotometer with KBr pellets. ¹H-NMR spectra were recorded with a JEOL 60 MHz NMR spectrometer in deuterated dimethylsulfoxide (DMSO-d₆), without internal reference. Differential scanning calorimetry measurements were performed with a Mettler DSC 12E at a heating rate of 10°C·min⁻¹ under nitrogen atmosphere. The thermal gravimetric analysis was carried out in air with a F Paulik Derivatograph at a heating rate of 12°C·min⁻¹. The number average molecular weights (M_n) and the polydispersity indices (M_w/M_n) of the copolymers were determined by gel permeation chromatography using a PL-EMD 950 Evaporative Mass Detector equipped with 2 × PLgel 5 μm MIXED-C, 300 × 7.5 mm columns. Optical polarized light microscopy investigations were performed with an Olympus BH-2 polarized light microscope fitted with a THMS 600/HSF91 hot stage, magnification 400x. The copolymers solubilities were determined at room temperature, at a concentration of 1 % (wt/v).

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