Research Article

Copolymers Formation by Photopolymerization of (Meth)acrylates Containing Dissolved Polyheteroarylenes

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Received 6 November 2008; Revised 19 February 2009; Accepted 27 April 2009

Recommended by Geoffrey R. Mitchell

Radical photopolymerization of (meth)acrylates in the presence of dissolved polyheteroarylenes has been investigated. The kinetics of radical polymerization of unsaturated monomers in the presence of polyheteroarylenes and model compounds has been studied by Differential Scanning Photocalorimetry and Infrared Spectroscopy. From the results of investigations into the kinetics and the polymer structures (Fourier Transform Infrared Spectroscopy, Nuclear Magnetic Resonance, Size-exclusion Chromatography, Thermogravimetric analysis), it has been established that radical photopolymerization of vinyl monomers in the presence of polyheteroarylenes leads to the formation of copolymers owing to chain transfer reactions and/or chain termination by the relevant condensation polymer. Using Electron Spin Resonance Spectroscopy the novel radicals upon the addition of model compounds for the polyheteroarylenes have been detected, and a mechanism of copolymer formation has been proposed.

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1. Introduction

Earlier we established that polyheteroarylenes (polyimides, aromatic polyesters, etc.) containing perfluoroalkylene, mainly $[\text{C}(\text{CF}_3)_2]$ moieties, and/or cardo groups have excellent solubility in organic solvents and several vinyl monomers (methyl methacrylate, ethyl acrylate, etc.). This served as the basis for studying the possibility of formulating new polymeric systems by polymerization of vinyl monomers containing dissolved polyheteroarylenes.

Research into the radical thermal polymerization of acrylates [1–4] and styrene [5] containing dissolved polyheteroarylenes (PHA), including the three-dimensional copolymerization of methyl methacrylate (MMA) with various difunctional monomers [6, 7], has shown the possibility to synthesize copolymers containing fragments of polyheteroarylenes and of carbon-chain polymers based on the vinyl monomers. In previous work using styrene as the vinyl monomer it has been established that the styrene

homopolymer is not formed even in the presence of only a small (4 wt%) content of polyimide (PI) in the monomer [5].

The photoinitiated polymerization of vinyl monomers in the presence of dissolved polyheteroarylenes has been investigated in order to define the universality of the above-stated approach to formation of copolymers. This research is also the result of new potential applications having opened for the photopolymerization processes including lithography [8], coatings [9], printed equipment, and nonlinear optics. [10–12]. Some previous interesting results on the photopolymerization of MMA in the presence of PI [13] also motivated us to pursue this research.

2. Experimental

2.1. Materials. Vinyl monomers, solvents, and monomers for the synthesis of polyheteroarylenes and model Diimide were purified by literature methods [3]. Photoinitiator (Pht) IRGACURE-1700 was supplied by CIBA-GEIGY

FIGURE 1: DSPC thermograms for photopolymerization. (a) 1: MMA, 2–4: MMA containing 5 wt.% of Diimide, PI 2 and PI 1; (b) MMA containing 5 (1), 10 (2), 20 (3), and 42 wt.% of PI 2 (4).

FIGURE 2: MMA conversion on irradiation time. 1: MMA + 5 wt% Pht, 2: MMA + 5 wt% Pht + 10 wt% PI 1, 3: MMA + 5 wt% Pht + 10 wt% Diimide.

FIGURE 3: FTIR spectra of Diimide (1), PMMA (2), and PMMA obtained in the presence of 20 wt.% of Diimide (3).

and used as received. Ethyl 2-bromopropionate, nitrosodurene (ND), 2-methyl-2-nitrosopropane (MNP), 2,2'-azo-bis-isobutyronitrile (AIBN), and $[\text{Re}(\text{CO})_5]_2$ were used as received from Aldrich or Acros Organics.

2.2. Polyheteroarylenes and Model Compounds. Synthesis of Diimide, PI, and polyarylate (PAr) is described in [4, 14]. In the present work we used PI 1 with $\eta_{\text{inh}} = 1.24 \text{ dL g}^{-1}$ (N-methylpyrrolidinone), PI 2 with $\eta_{\text{inh}} = 0.29 \text{ dL g}^{-1}$ (dimethylformamide), and PAr with $\eta_{\text{inh}} = 0.71 \text{ dL g}^{-1}$ (N-methylpyrrolidinone).

2.3. Differential Scanning Photocalorimetry (DSPC). DSPC studies were performed on a DuPont 930 apparatus with a double heat differential calorimeter 912. Used experimental technique was given in details [13]. The average of two obtained kinetic results values with the calculated error is presented in the tables because of high sensitivity of a Differential Scanning Photocalorimeter.

2.4. Real-Time Infrared Spectroscopy (RT-FTIR). Real-Time Fourier-Transform Infrared (RT-FTIR) spectra were obtained with "Spectrum GX System FTIR spectrometer, Perkin Elmer Instruments." This method allows estimation of the polymerization kinetics by measuring the reduction in intensity of absorption bands typical to double bonds in the monomer: C–H out-of-plane vibrations at double bond and stretching vibrations of C=C bond.

2.5. Bulk Photopolymerization. The solutions of monomers containing Pht (3 wt.% or 5 wt.%) and various additives were exposed to UV-irradiation with light intensity of 31.5 mW cm^{-2} . Polymerization was carried out at room temperature; irradiation time was 30 minutes.

FIGURE 4: ^1H NMR spectra of Diimide (1), PMMA (2), and PMMA obtained in the presence of 20 wt.% of Diimide (3).

The maximum quantity of an additive compound was limited by the solubility of the monomer, and the viscosity of the monomer solution obtained. To achieve better homogenization the Pht was introduced first, and the PHA was then added. Polymers obtained from polymerization of methyl methacrylate were isolated by the precipitation from chloroform solution using methanol. The polymers were dried under vacuum at 70–80°C. The isolation of polymers using ethyl acrylate (PEA) as vinyl monomer was carried out by the evaporation of chloroform from polymer solutions in a Petri dish.

2.6. Characterization Methods and Property Measurements. ^1H and ^{13}C NMR spectroscopy analysis was performed on a Bruker-AC 250 MHz using CDCl_3 as the solvent.

Dynamic thermogravimetric analysis (TGA) was performed in nitrogen atmosphere on a analyzer TGA Q50 at the heating rate 5°C min $^{-1}$.

Size exclusion chromatography (SEC) analyses of the samples were carried out on a Spectra Physics apparatus, using polystyrene standards for calibration and tetrahydrofuran as a carrier solvent at 30°C with a flow rate of 1 mL min $^{-1}$.

2.7. Electron Spin Resonance (ESR). ESR spectra were recorded on a Varian E-12A spectrometer. The required quantity of AIBN, ND, MNP, Diimide, or phenyl benzoate was dissolved in a small amount of dichloromethane or in a mixture of dichloromethane with the monomer (EA or styrene). Reaction solutions were degassed in glass vials and irradiated at ~20°C using a DRSh-1000 lamp directly in the

resonator of the spectrometer. A band with $\lambda = 366$ nm was isolated through a glass color filter. The standard of firm “Varian” $g = 2.0028$ has been utilized as the standard for calculation of g -factors of identified radicals. Spectra have been simulated using the program “SimFonia.”

3. Results and Discussion

MMA and ethyl acrylate (EA) were used, as vinyl monomers. High (PI 1) and low molecular (PI 2) weight polyimides, polyarylate (PAr), and Diimide have been investigated as the compounds added to the monomers.

3.1. Photopolymerization of MMA and EA in the Presence of PIs, PAr, and Diimide. Weight ratio of PI and MMA was varied from 5 : 95 to 42 : 58. The amount of PI 1 and PI 2 introduced was no more than 15 wt.% and 42 wt.%, respectively, and was limited by the extremely high viscosity of the resulting monomer solutions containing PI. Polymerization of MMA in the presence of model compound (Diimide) has been investigated in order to determine the exact PI chemical species involved in the MMA photopolymerization.

PAr was also used as the additive in spite of its low solubility (only 5 wt% PAr was soluble in MMA), to compare the influence of various PHA on the kinetics of unsaturated monomer photopolymerization and on the properties of polymer systems formed.

Autocatalytic model have been used for determination of kinetic parameters. This method is described in details in [15].

The added compounds influence strongly the kinetic curves of MMA polymerization. Thus, the rate of polymerization decreases in series PI 1 > PI 2 > Diimide (Figure 1(a)). It has been shown by the example of addition of PI 2 that the rate of polymerization decreases as the amount of compound introduced into the monomer solution increases from 5 wt.% up to 42 wt.% (Figure 1(b)). It is evident that viscosity is not the only factor that influences the kinetics of MMA polymerization. Most likely, the interactions of the growing PMMA radical and/or a radical formed upon decomposition of Pht by molecules of the added compound also influence the kinetics of MMA polymerization. As a result less reactive radicals are formed which reduce the MMA polymerization rate in the presence of these compounds. Thus, Diimide and PI 2 decrease, but PI 1 accelerates the process of MMA polymerization. Apparently, this latter effect is determined by the viscosity factor which results in an increased polymerization rate with an insignificant content of high molecular PI 1.

Activation energy of reaction (E_a) has been calculated from experimentally obtained temperature dependence of polymerization rate constants (Table 1), using the Arrhenius equation. The determined value of activation energy for MMA polymerization (8.1 kJ mol $^{-1}$) has the good agreement with results published by Lecamp et al. (2.2 kcal mol $^{-1}$ = 9.2 kJ mol $^{-1}$) [16]. The difference in 0.9 kJ mol $^{-1}$ is probably due to using bifunctional monomer in the paper cited above.

TABLE 1: The rate constants of MMA and EA photopolymerisation in the presence of Diimide, PI 1, and PI 2 determined by DSPC.

Monomer	Parameter	—	Added compound											
			Diimide, wt%			PI 1, wt%			PI 2, wt%					
	at T, °C		5	10	20	42	5	10	5	10	20	42		
MMA	k, min ⁻¹	30	0.68 ± 0.03	0.53 ± 0.04	0.52 ± 0.02	0.56 ± 0.07	0.39 ± 0.04	0.72 ± 0.00	0.72 ± 0.14	0.45 ± 0.02	0.42 ± 0.01	0.45 ± 0.07	0.28 ± 0.02	
		40	0.80 ± 0.01	0.72 ± 0.01	0.61 ± 0.02	0.65 ± 0.10	0.54 ± 0.07	0.75 ± 0.02	0.72 ± 0.16	0.52 ± 0.09	0.44 ± 0.05	0.53 ± 0.05	0.28 ± 0.01	
		50	0.81 ± 0.01	0.71 ± 0.11	0.53 ± 0.10	0.58 ± 0.00	0.45 ± 0.01	0.79 ± 0.07	0.89 ± 0.20	0.59 ± 0.11	0.47 ± 0.08	0.52 ± 0.07	0.27 ± 0.06	
		60	0.83 ± 0.14	0.84 ± 0.01	0.68 ± 0.12	0.74 ± 0.04	0.50 ± 0.05	0.78 ± 0.06	0.73 ± 0.05	0.48 ± 0.09	0.45 ± 0.02	0.58 ± 0.07	0.41 ± 0.08	
		70	1.02 ± 0.03	0.65 ± 0.02	0.67 ± 0.08	0.56 ± 0.02	0.45 ± 0.02	0.98 ± 0.12	0.74 ± 0.02	0.62 ± 0.05	0.61 ± 0.00	0.60 ± 0.08	0.47 ± 0.02	
EA	k, min ⁻¹	30	1.61 ± 0.34	1.23 ± 0.20	1.71 ± 0.03	2.04 ± 0.21	1.88 ± 0.33	1.62 ± 0.07	1.67 ± 0.14	1.24 ± 0.13	0.97 ± 0.10	0.84 ± 0.02	1.36 ± 0.08	
		40	1.69 ± 0.40	1.27 ± 0.32	1.77 ± 0.06	1.94 ± 0.29	1.77 ± 0.16	1.69 ± 0.03	1.64 ± 0.02	1.10 ± 0.08	0.95 ± 0.01	0.88 ± 0.05	1.43 ± 0.49	
		50	1.98 ± 0.09	1.36 ± 0.36	1.90 ± 0.15	2.21 ± 0.06	1.84 ± 0.06	1.75 ± 0.09	1.77 ± 0.43	1.24 ± 0.21	1.07 ± 0.05	0.84 ± 0.01	1.51 ± 0.17	
		60	1.84 ± 0.01	1.40 ± 0.07	2.08 ± 0.07	2.16 ± 0.09	1.86 ± 0.25	1.69 ± 0.04	1.64 ± 0.24	1.41 ± 0.08	1.21 ± 0.14	0.99 ± 0.08	1.41 ± 0.15	
		70	2.31 ± 0.08	1.58 ± 0.35	2.17 ± 0.14	2.27 ± 0.17	2.14 ± 0.14	1.98 ± 0.18	1.73 ± 0.39	1.58 ± 0.28	1.22 ± 0.03	1.08 ± 0.08	1.40 ± 0.20	

As can be seen from Table 2, introduction of additives to MMA involves a reduction of the polymerization activation energy. Increasing their content in the initial mixture results in the further decrease of E_a . Nevertheless, behavior specific to each introduced compound has been observed. On the one hand a more than sixfold reduction of E_a was obtained, using as an additive 10 wt% of PI 1 (maximum possible concentration), compared to the E_a for pure MMA. On the other hand, addition of the maximum possible amount of PI 2 (42 wt%) drastically increases the E_a of MMA photopolymerization.

A peculiar conduct of the solutions containing various amounts of Diimide has been observed. A marked reduction of E_a of MMA polymerization takes place upon introduction 5 wt% of Diimide (Table 2). An increase in the content of Diimide causes only a slight further decrease of E_a .

In our earlier work it was shown that both PAr and PI cause significant changes in the kinetics of thermal polymerization of vinyl monomers [4] and in the properties of the polymers formed [3, 5].

The results of a kinetic parameters calculation for MMA polymerization in the presence of PAr do not allow us to compare it unambiguously with those for the PI systems. For instance, rate of MMA polymerization increases to a greater degree upon introduction of PAr (5 wt%) than upon addition of PI 1 to the system. E_a of this system, compared to E_a of pure MMA, increases only in the presence of Pht as has been observed exclusively earlier when using 42 wt% of PI 2 (Table 2).

The MMA polymerization results obtained by the calorimetric study correlate well with those obtained by RT-FTIR.

For (meth)acrylates the characteristic bands are at 812 cm^{-1} (out-of-plane vibrations of C-H at double bond) and 1635 cm^{-1} (stretching vibrations of double bond C=C) [17–19]. The conversion of MMA upon irradiation has been calculated via absorbance intensity of the band at 1635 cm^{-1} . One can see from Figure 2 (curve 2) that the introduction 10 wt% of PI 1 leads to a drastic increase in the polymerization rate while the addition 10 wt% of Diimide markedly slows down the photopolymerization of MMA (curve 3), which agrees absolutely with the results from DPC.

It is known that EA has a higher reactivity than MMA and that it can dissolve PI. Polyethylacrylate (PEA) is an elastomer, so that both the homopolymer and its different copolymers find applications in various areas [20].

Using DSPC it has been established that the rate of EA photopolymerization in the presence of PI 2 and Diimide reduces, whereas the addition of PI 1 leads to increasing the polymerization rate due to the viscosity factor as was observed at the photopolymerization of MMA.

Dissolving 5 wt% of Diimide in the monomer results in the reduction of kinetic parameters of EA polymerization. However with increasing Diimide concentration the reaction constants of EA polymerization raise, which was not observed for photopolymerization of MMA. The concentration of PI 1 has no significant influence on the rate constant for EA polymerization (cf. the similar results for MMA).

E_a of EA polymerizations decreases with an increase in the content of the dissolved compound and achieves the

minimum value at the maximum amount of such compound (the only exception being the solutions with Diimide; see Table 2). The general tendency for E_a to decrease with increasing content of Diimide is observed, despite the irregularity of this reduction.

The growing PEA radical is probably less sterically hindered than the PMMA radical, which promotes its interaction with molecules of added compounds, including Diimide, and so produces greater changes in the kinetics of EA polymerization.

To prove the formation of new radicals (participation of PHA) during the initiation and/or termination steps of the polymerization of vinyl monomers, the ESR spectroscopy technique of spin traps was utilized [21]. Diimide and phenyl benzoate were used as model compounds of PI and PAr, respectively. The results obtained are presented in Table 3. It has been established that the addition of phenyl benzoate and Diimide results in the formation of new radicals which differ in their magnetic resonance parameters from the radicals which are detected in a reaction system without Diimide and phenyl benzoate. These radicals represent the secondary carbon-centered or acyl radicals which are caught by a spin trap (Table 3).

Thus, the results of ESR spectroscopy have confirmed the previously proposed [4] mechanism of copolymer formation by the interaction of reaction system radicals with functional groups of the PHA added to the monomer. The parameters of detected radicals are similar to those published earlier in [22–25].

3.2. Characterization of (Co)polymers Based on PMMA and PEA Obtained in the Presence of PI, PAr, and Diimide. Since Diimide does not precipitate when a large excess of methanol is added to the solution of the polymer, reprecipitation of the latter from chloroform with methanol, followed by multiple washing, should remove all unreacted Diimide. The study of the model system PMMA – 20 wt% of Diimide by FTIR has revealed changes in the spectra caused by Diimide, namely, an increased intensity of absorbance at $1370\text{--}1385\text{ cm}^{-1}$ owing to the $\text{--N} < \text{imide cycle}$ (Figure 3).

The presence of Diimide in the obtained mixture PMMA and Diimide is also confirmed by ^1H and ^{13}C NMR (Figures 4 and 5): signals from Diimide being seen at 7.3–8.3, 120–140, and 165–166 ppm, respectively.

However, not all the Diimide added to the monomer takes part in the chemical interaction, as shown by comparison of the ^1H and ^{13}C NMR spectra of PMMA obtained in the presence 20 wt% of Diimide and a corresponding mechanical blend. The quantity of Diimide that reacted during the polymerization of MMA has been calculated by the comparison of peak intensities of Diimide, in the ^1H and ^{13}C NMR spectra for PMMA synthesized in the presence of Diimide, and the corresponding mixture of PMMA and Diimide. This value has been established to be $5.3 \pm 1.2\text{ wt\%}$ (on PMMA). These results are in good accordance with the element analysis data for fluorine content: F is calculated (for 100 wt% PMMA plus 20 wt% Diimide) and found to be 3.20 wt.% and 0.78 wt.%, respectively; that is, the content of Diimide in modified PMMA is 4.9 wt%. Incomplete

TABLE 2: Activation energy of MMA and EA photopolymerization in the presence of DI, PI 1, PI 2, and PAr.

Added compound, wt.%		E_a , kJ mol ⁻¹	
		MMA	EA
—	—	8.14 ± 0.62	6.99 ± 0.15
PI 1	5	6.08 ± 0.69	3.21 ± 0.22
	10	1.27 ± 0.17	0.96 ± 0.26
PI 2	5	7.19 ± 0.48	6.68 ± 0.48
	10	6.48 ± 0.15	6.39 ± 0.32
	20	6.10 ± 0.48	5.57 ± 0.31
	42	12.11 ± 1.22	0.34 ± 0.04
Diimide	5	5.00 ± 0.02	4.61 ± 0.37
	10	4.78 ± 0.44	5.35 ± 0.05
	20	4.00 ± 0.17	2.16 ± 0.60
	42	4.42 ± 0.30	3.13 ± 0.45
PAr	5	11.25 ± 0.90	—

TABLE 3: ESR spectra data of nitroxyl radicals detected at irradiation of studied solutions. Solvent—CH₂Cl₂; [Styrene]₀, [Phenyl benzoate]₀, [Diimide]₀, [Ethyl acrylate]₀ = 1 mol L⁻¹; [AIBN]₀, [MeCHBrC(O)OEt]₀, [Re₂(CO)₁₀]₀ = 3 × 10⁻³ mol L⁻¹.

Radical source	Spin-Trap	Detected radical	Hyperfine splitting Constants (G)		g-Value
			a _N	a _{β-H}	
Styrene	ND*	Me ₂ *CCN (R)	12.8	—	2.0059
AIBN		RCH ₂ *CHPh	13.7	4.0	2.0059
Styrene	ND	R	12.8	—	2.0059
AIBN		PhCOCH ₂ *CHPh	13.7	5.2	2.0061
Phenyl benzoate		O*CPh	7.2	—	2.0069
AIBN	ND	R	12.8	—	2.0059
Phenyl benzoate		O*CPh	7.2	—	2.0069
Phenyl benzoate	MNP**	O*CPh	8.0	—	2.0066
		PhC(O)O*C ₆ H ₅	14.2	2.7	2.0060
Styrene	ND	A***	13.7	8.2	2.0060
AIBN		B***	13.7	4.2	2.0060
Diimide					
AIBN	ND	R	12.9	—	2.0060
Diimide		B***	13.8	4.0	2.0060
		O*CPh	5.4	—	2.0064
Diimide	MNP	*Bu ^t	15.7	—	2.0060
		B***	15.0	3.7	2.0060
AIBN	ND	R	12.8	—	2.0059
Ethyl acrylate		RCH ₂ *CHC(O)OEt	13.6	8.0	2.0059
MeCHBrC(O)OEt	ND	A***	13.6	8.2	2.0059
Re ₂ (CO) ₁₀		B***	13.6	4.0	2.0059
Diimide					

* Nitrosodurene (ND)

** 2-Methyl-2-nitrosopropane (MNP)

*** see the scheme and text.

PI 1 ($\eta_{inh} = 1.24$ dL/g (MP))

PI 2 ($\eta_{inh} = 0.29$ dL/g (DMF))

PAr ($\eta_{inh} = 0.71$ dL/g (MP))

Diimide

SCHEME 1

SCHEME 2

SCHEME 3

FIGURE 5: ^{13}C NMR spectra of Diimide (1), PMMA (2), and PMMA obtained in the presence 20 wt.% of Diimide (3).

interaction of Diimide with the radicals, formed during the photoinitiated polymerization of MMA, is also indicated by kinetic investigations.

It is necessary to pay attention to some features of the polymers based on PEA. Thus, for photopolymerization of EA containing PI 2 (20 wt.% and 42 wt.%) and PI 1 (5 wt.%), the samples obtained are gel-like polymers soluble in chloroform only at intense stirring. However, the gel containing 11 wt.% of PI 1 cannot be dissolved. Probably, the three-dimensional network formation is due to repeated addition of a growing PEA macroradical to molecules of introduced compound as well as to multiple participation of PI macromolecules in this process.

At the same time the polymer samples, containing 20 wt.% and 42 wt.% of PI 2, are precipitated upon adding a chloroform solution to methanol. The presence of PEA in each sample is confirmed by the FTIR spectra which show the characteristic bands for PEA at 2981, 1177, 1161, 1025, and 853 cm^{-1} (Figure 6). It should be noted that unmodified PEA is not precipitated from a chloroform solution by methanol.

The polymer samples obtained in the presence of Diimide, PI 1, and PI 2 are differed in an increased thermal stability, compared to pure PMMA and PEA (Table 4). As one can see from the results given in Table 4 even the addition of 5 wt.% model Diimide, PI 1, PI 2, or PAr results in an increase in the 10% weight loss temperature ($T_{10\%}$) for these sample on 35, 50, 60, and 20°C, compared to unmodified PMMA. The maximum increase of $T_{10\%}$ (85°C) is achieved when 42 wt.% of PI 2 is added.

The mechanical blends of PMMA and 20 wt.% of Diimide, PMMA, and 20 wt.% of PI 2 prepared from common solutions have precisely the same $T_{10\%}$ as unmodified

TABLE 4: 10% weight loss temperature of polymers obtained by polymerization of MMA and EA in the presence of DI, PI 1, PI 2, and PAr.

Added compound, wt%		T _{10%} (°C) of (co)polymer based on:	
		PMMA	PEA
—	—	210	320
Diimide	5	245	335
	10	245	335
	20	250 (210)*	340
	42	225	330
	5	260	345
PI 1	10	250	345 (345)**
	15	270	—
	5	270	345
PI 2	10	270	345
	20	280 (210)*	350
	42	295	340 (345)***
PAr	5	230	—
Diimide		335****	
PI 1, PI 2		525****	
PAr		470****	

For the comparison T_{10%} of

*Homopolymers mixture prepared from common solution;

**Gel fraction;

***Copolymer precipitated from chloroform solution into methanol;

****Used PHA and Diimide.

TABLE 5: SEC results of polymers based on MMA and EA.

Sample	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
PMMA*	12.6	27.8	2.2
MMA + 20 wt.% Diimide	21.9	49.4	2.3
MMA + 10 wt.% PI 1	28.6	96.7	3.4
MMA + 20 wt.% PI 2	31.6	75.7	2.4
MMA + 5 wt.% PAr	16.0	34.6	2.2
PEA*	39.7	107.6	2.7
EA + 11 wt.% Diimide	56.2	143.1	2.6
EA + 42 wt.% Diimide	62.6	138.4	2.2
EA + 5 wt.% PI 1	86.9	348.4	4.0
EA + 11 wt.% PI 1	70.3	252.2	3.6
EA + 5 wt.% PI 2	50.9	269.2	5.3
EA + 11 wt.% PI 2	24.9	200.6	8.1
EA + 20 wt.% PI 2	42.6	300.1	7.0
EA + 42 wt.% PI 2	55.1	300.2	5.5
PI 1*	186.7	345.5	1.9
PI 2*	31.5	54.0	1.7
PAr*	54.5	99.9	1.8

*For the comparison.

PMMA. Therefore, it can be concluded that this increase in the thermal stability of PMMA is due to the formation of copolymers and to extra intermolecular interactions.

The addition of PI 1, PI 2, and FI results in an increase of thermal stability of the copolymers, but not so significant as

for PMMA (Table 4). The maximum increase of T_{10%} is 30°C at addition of 20 wt% of PI 2.

It is known that the mechanism of PEA thermal decomposition is not the same as the PMMA depolymerization process [26, 27]. Therefore, the most likely reason of the

FIGURE 6: FTIR spectra of PEA (1), PI 2 (2), and PEA obtained in the presence 42 wt% of PI 2 and precipitated into methanol (3).

FIGURE 7: Chain-length distribution of PMMA obtained by photopolymerization of MMA in the presence 10 wt% of PI 1 (1) and relevant mixture (2).

increased thermal stability of polymeric samples based on PEA is the intermolecular interactions of PEA with Diimide, PI 1, and PI 2 rather than copolymer formation.

Molecular weights and polydispersity of the synthesized (co)polymers are given in Table 5. It should be noted that introduction of PI 1, PI 2, and PAr as well as the addition of Diimide results in the formation of higher molecular weight products from MMA polymerization. In this context, the polydispersity of the copolymers obtained increases (the exception is the sample containing 5 wt% of PAr). The higher polydispersity, most likely, indicates the formation of branched copolymers. Another confirmation of copolymer formation has been established by SEC for

PMMA with 10 wt% of PI 1 having a unimodal molecular weight distribution (MWD) in comparison with bimodal MWD for the corresponding mechanical blend (Figure 7).

It has been established that introduction of Diimide into EA results in the formation of polymers with higher molecular weights and lower polydispersity. The addition of PI owing to the obtaining branched copolymers (see above) promotes the formation of polymer systems, which are characterized by a much higher polydispersity index than unmodified PEA or PI itself.

4. Conclusion

It has been established by Fourier IR, NMR, SEC, and TGA methods that the radical photopolymerization of (meth)acrylates in the presence of dissolved polyheteroarylenes produces novel copolymers. The kinetic parameters of radical polymerization of unsaturated monomers in the presence of polyheteroarylenes and model compounds have been investigated by differential scanning photocalorimetry and IR spectroscopy. Using ESR spectroscopy novel radicals obtained by the addition of model compounds of polyheteroarylenes have been detected and a mechanism for the formation of copolymers has been proposed. The resulting copolymers have superior thermal properties to the relevant carbon-chain homopolymers.

Acknowledgment

D. A. Sapozhnikov gratefully acknowledges the French embassy in Russia for the support in carrying out the investigations in LEMP/MAO (University Montpellier 2) by the program "cotutelle."

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