Kinetic Study of a New Flame-Retardant Polymer Composition

TRAIAN ROTARIU[1], TEODORA ZECHERU[2,3,*], EDINA RUSEN[2], DORU-ADRIAN GOGA[1], CORNELIU CINCU[2]
[1]Military Technical Academy, 81-83 George Coşbuc Blv., 050141, Bucharest, Romania
[2]University Politehnica of Bucharest, 149 Calea Victoriei, 010072, Bucharest, Romania
[3]NBC Defense and Ecology Scientific Research Center, 225 Şos. Olteniţei, 041309, Bucharest, Romania

Safety requirements are becoming more and more important in terms of polymers interaction with fire, while various flame retardant additives are being expelled for their adverse effects on the environment. This is the reason for the research challenge for new effective and environmentally friendly flame retardant systems. In this view, the objectives of the present study were the synthesis of the 2,4,6-triiodophenyl acrylate (TIPA) monomer and of p(MMA-co-TIPA) copolymer; and the determination of the reactivity ratios of the comonomers. As foreseen, MMA reactivity is obviously superior to TIPA ($r_1 = 5.49$ and $r_2 = 0.053$), and a decrease of initial copolymerisation rate is noticed as the feed enriches in MMA.

Keywords: reactivity ratio, 2,4,6-triiodophenyl acrylate, homopropagation

The wide use of polymer materials in our everyday life is due to their remarkable combination of properties, low weight and ease of processing. Safety requirements are currently becoming more and more important in terms of polymers interaction with fire and their fire resistance performances, while various flame retardant additives, such as some halides, are being expelled for their suspected adverse effects on the environment. This is the reason for the research challenge for new effective and environmentally friendly flame retardant systems [1].

Homopolymer and copolymers of methylmethacrylate (MMA) are widely used in various fields of application, such as medicine, due to their established biocompatibility [2-4]. Poly(methylmethacrylate) (pMMA) is also used as an alternative to glass, as ocular lenses or aquariums, and in competition with polycarbonate it is preferred for its moderate properties, easy handling and processing at low cost [5-6].

Another interesting application of pMMA is its use in the field of optics, for daylight redirection and attenuation, or as a shield to stop beta radiation emitted from radioisotopes [7-11]. Unfortunately, pMMA behaves in a brittle manner when loaded, especially under an impact force. Moreover, in order to be used in flame retardant materials [12], it is preferred to be used in combination with another comonomer, in order to satisfy some important requirements: unharmful for the environment, halide-containing and chemically compatible.

The advantages of using bromide and chloride-compounds in fire extinguishing compositions are: excellent flame retardant capacity, due to the inhibition of the flame propagation mechanism and high chemical stability. The latter one represents also a great disadvantage, due to their long life in the environment; under the influence of ultraviolet radiation, chlorides and bromides are decomposed to their radicals, which destroy the ozone [1, 13-14].

This is the reason for their complete removal from use. Nowadays, researches are focused on the improvement of other compositions, in terms of efficiency together with environment compatibility. Aerosol particles offer a good solution to this matter, their diameter (20-60 μm) being related to a small surface/volume ratio.

For the present study a iodine-based acrylate was chosen, which is used in optical materials with a high refractive index [15-16]; it also appears to be excellent in polymerizations with ultraviolet radiations and electron beams and it could be used in flame retardant polymeric compounds, etc. [1, 17-18]. The possible role of iodine-containing compounds in the enhancement of mercury depletion is also considered [19].

There were synthesized copolymers of MMA and 2,4,6-triiodophenyl acrylate (TIPA). The copolymers exhibit good environment compatibility, taking into consideration that they are also biocompatible. TIPA is a very convenient monomer, as it is very easy to synthesize and purify.

In the present study, the relationship between the monomers composition in the feed and in the copolymer was examined. The reactivity ratios of the two monomers were determined by the most common integral and differential equations.

Experimental part
Materials and methods

MMA (Aldrich) was used after a preliminary purification by vacuum distillation (63°C and 200 mmHg). Benzoyl peroxide (BPO) (Aldrich) was purified through recrystallization from methanol at 45°C. Acryloyl chloride (AC) (Merck), 2,4,6-triiodophenol (TIP) (Aldrich), dichloromethane (DCM) (Merck) and triethylamine (TEA) (Merck) was used as supplied. Tetrahydrofuran (THF) (Merck) was purified by distillation, in the following way: first, it was distilled on cuprous chloride ($CuCl_2$), then the medium fraction was deposited overnight on potassium hydroxide pellet (KOH) and finally it was rectified over metallic sodium (66.8°C).

Synthesis of TIPA

The synthesis reaction (fig. 1) was adapted from a method previously described in the literature [20]. In brief, 1.9 mL (0.022 moles) of AC were dissolved in 70 mL DCM and the mixture was added dropwise under stirring to a mixture of 10 g (0.019 moles) TIP and 2.64 mL (0.019 moles) TEA dissolved in 100 mL DCM. The solution was stirred below room temperature and kept for 4 h. The resultant compound, TIPA, was collected from the organic phase. The monomer obtained, TIPA, was washed with 10% (in weight) $NaHCO_3$, 10% (in weight) NaCl three times each and then dried over anhydrous Na_2SO_4. The product

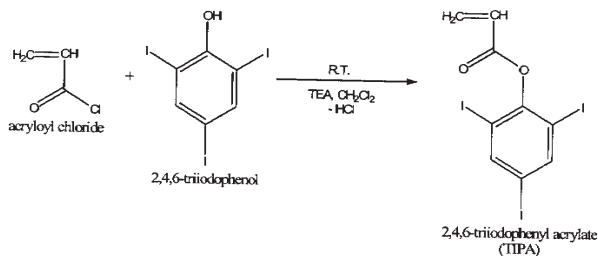** email: teodora.zecheru@yahoo.com. Tel.+40213364591*
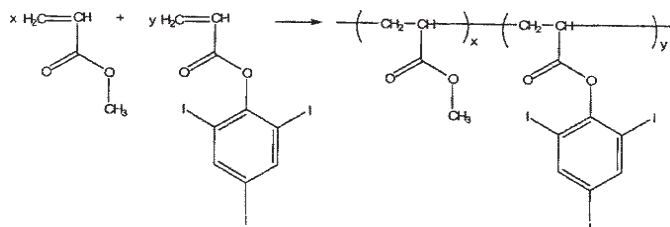
Fig. 1.Chemical synthesis of TIPA monomer

Fig. 2. Chemical structure of p(MMA-co-TIPA) copolymer

Table 1
FEED COMPOSITIONS OF THE BINARY
SYSTEMS

Composition	Monomer 1 (MMA)	Monomer 2 (TIPA)
1	0.2	0.8
2	0.4	0.6
3	0.6	0.4
4	0.8	0.2

10 mmHg. The yield of the obtained light yellow product was approximatively 82%.

Synthesis of MMA-TIPA copolymers

For bulk copolymerization (fig. 2), the monomers and the initiator (BPO = 10^{-2} mole/L) were mixed together by vortexing at 30 Hz, then introduced into glass vials. Polymerizations were carried out in inert atmosphere, at 75°C, and samples were extracted at well-defined periods of time. The obtained polymers were precipitated with THF, dried and weighted.

For the determination of the reactivity ratios of the binary system MMA-TIPA, copolymerizations were performed at different compositions in the feed (table 1). For each feed composition, there were extracted samples at different reaction time periods and conversions were determined.

Characterizations techniques of the copolymers

ATR-FTIR spectra of the copolymers were obtained at 20°C and constant 40% relative humidity by coupling ATR modulus to a Bruker Vertex 70 spectrophotometer. Spectra were obtained over the range of 4000–350 cm^{-1} at 4 cm^{-1} resolution and the number of scans 50.

The copolymers were subjected to elemental analysis using a C, H, N analyzer EAGER 200, Stripchart.

Results and discussions

The first approach of the study was to confirm the TIPA structure (shown in fig. 1) through ATR-FTIR. Spectrum analysis lead to the observation of characteristic peaks: C-I stretching vibrations appear in the interval of 550-650 cm^{-1}, as a range of weak and medium peaks, while =C-H and =CH_2 from alkene function are observed at 3049 cm^{-1} and C=C sp^2 from phenyl-ring at 1529 cm^{-1} (stretching vibrations), C-H bending and ring puckering at 793; and a strong band of C=O (stretching vibrations) from ester functional class at 1743 cm^{-1}. 1135 and 1205 cm^{-1} represent the 2-band stretching vibration O-C bond from ester functional class. At 859 cm^{-1} appears the C-O-C bond from ether functional class.

In comparison with the spectrum of TIPA, in the spectra of the p(MMA-co-TIPA) copolymers the peak at 3049 cm^{-1} disappears, and the ones at 2945 cm^{-1}, representing CH_3, CH_2 and CH stretching vibrations and 1420 and 1360 cm^{-1} from CH_2 and CH_3 deformation of alkanes, increases.
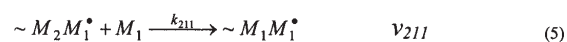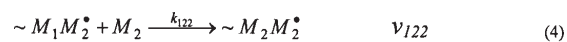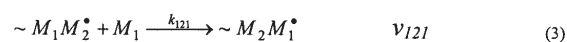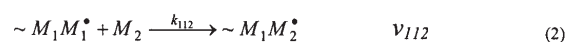
The peak at 1538 cm^{-1} increases with the ratio of TIPA following a gain in phenyl functions (C-C sp^2). The C=O peak at 1725 cm^{-1} from the ester function, is displaced due to steric effects by polymerisation of the two esters, one being a methacrylate-ester and the other - an acrylate-ester. The spectra show that iodine bonds C-I are also present in the monomer and in the copolymer, due to the peaks at 701, 668, and 566 cm^{-1}; in the same time, the peak in the monomer for ether functional group at 859 cm^{-1} is displaced to 862 cm^{-1} (C-O-C bending vibrations).

The copolymers obtained were submitted to elemental analysis, in order to determine their molar composition. The results are given in table 2 and 3. The copolymer is composed of C, H, O and I; therefore, the difference up to 100% from the elemental analysis in table 2 is represented by the total amount of oxygen and iodine.

In table 3, knowing the difference between the molecular weight between the monomers (MMA = 100 g/mole and TIPA = 399 g/mole), and the total ratio of C and H in the copolymer, by applying the relationship for the determination of the bulk formula, the ratio and the composition of the copolymer obtained are established using a 1st order equation.

Knowing the composition in the feed, as well as the composition of the obtained copolymers and the corresponding conversions, the PROCOP software allows the determination of the reactivity ratios [21]. The penultimate model was considered in the kinetic model (8 types of propagation reactions) due to sterical effects (volume of TIPA comonomer), which affects the macroradicals reactivity.

The kinetic scheme is presented below, in equations (1)-(8) (where M_1 = [MMA] and M_2 = [TIPA], k_i = reactivity constants; v_i = reactivity ratios).

$$\sim M_1 M_1^\bullet + M_1 \xrightarrow{k_{111}} \sim M_1 M_1^\bullet \qquad v_{111} \qquad (1)$$

$$\sim M_1 M_1^\bullet + M_2 \xrightarrow{k_{112}} \sim M_1 M_2^\bullet \qquad v_{112} \qquad (2)$$

$$\sim M_1 M_2^\bullet + M_1 \xrightarrow{k_{121}} \sim M_2 M_1^\bullet \qquad v_{121} \qquad (3)$$

$$\sim M_1 M_2^\bullet + M_2 \xrightarrow{k_{122}} \sim M_2 M_2^\bullet \qquad v_{122} \qquad (4)$$

$$\sim M_2 M_1^\bullet + M_1 \xrightarrow{k_{211}} \sim M_1 M_1^\bullet \qquad v_{211} \qquad (5)$$

Composition	Conversion (%)	Δ t (min.)	Elemental analysis		
			N (%)	C (%)	H (%)
1	0.3470	15	0	26.967	2.187
1	0.6924	35	0	26.447	2.185
1	0.7892	60	0	25.329	2.244
2	0.2781	20	0	28.692	3.181
2	0.4778	40	0	25.287	3.670
2	0.56	60	0	27.190	3.826
3	0.2028	20	0	41.710	4.442
3	0.4529	50	0	52.320	0
3	0.6135	120	0	31.431	3.530
4	0.2036	20	0	39.773	5.443
4	0.3963	40	0	40.501	5.248
4	0.4933	60	0	40	5.680

Table 2
RESULTS OF THE ELEMENTAL ANALYSIS FOR THE BINARY SYSTEM MMA-TIPA

x_{MMA}*	x_{TIPA}*	%C	%H	X_{MMA}**	X_{TIPA}**
0.2	0.8	58.297	9.056	0.5454	0.4545
0.2	0.8	49.112	9.144	0.5633	0.4367
0.2	0.8	32.397	8.791	0.6296	0.3734
0.4	0.6	28.692	3.181	0.8379	0.1621
0.6	0.4	41.710	4.442	0.8016	0.1984
0.6	0.4	31.431	3.530	0.8500	0.1500
0.8	0.2	40.501	5.248	0.9753	0.0247

Table 3
CALCULATED MOLAR RATIOS FOR THE BINARY SYSTEM MMA-TIPA

*composition of the monomers in the feed;

**composition of the copolymer from elemental analysis

was separated from DCM by rotoevaporation at 30°C and

$$\sim M_2 M_1^{\bullet} + M_2 \xrightarrow{k_{212}} \sim M_1 M_2^{\bullet} \qquad v_{212} \qquad (6)$$

$$\sim M_2 M_2^{\bullet} + M_1 \xrightarrow{k_{221}} \sim M_2 M_1^{\bullet} \qquad v_{221} \qquad (7)$$

$$\sim M_2 M_2^{\bullet} + M_2 \xrightarrow{k_{222}} \sim M_2 M_2^{\bullet} \qquad v_{222} \qquad (8)$$
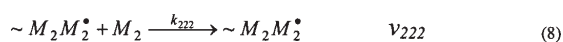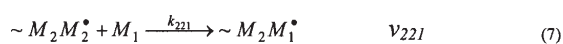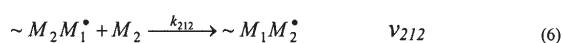
The consumption rates of the two monomers being known, respectively admitting that the concentration of each type of propagating radical is constant, the following equation is obtained (9) [22]:

$$\frac{dM_1}{dM_2} = \frac{1 + r_{21} \dfrac{M_1}{M_2} \cdot \dfrac{r_{11} M_1 + M_2}{r_{21} M_1 + M_2}}{1 + r_{12} \dfrac{M_2}{M_1} \cdot \dfrac{r_{22} M_2 + M_1}{r_{12} M_2 + M_1}} \qquad (9)$$

where $r_{11} = \dfrac{k_{111}}{k_{112}}$, $r_{21} = \dfrac{k_{211}}{k_{212}}$, $r_{12} = \dfrac{k_{122}}{k_{121}}$, $r_{22} = \dfrac{k_{222}}{k_{221}}$ (r_i = reactivity rations).

The values obtained using the PROCOP software were: r_{11}=4.89, r_{22}=0.051, r_{21}=31.83, r_{12}=0.053
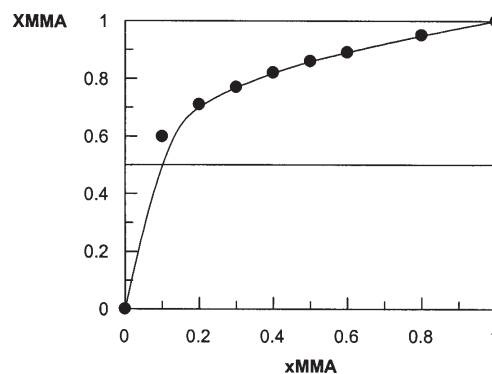

Fig. 3 - Composition diagram of the binary system MMA-TIPA

Following the reactivity ratios obtaining, the composition diagram for the binary system MMA-TIPA can be drawn (fig. 3).

The conclusion drawn from the analysis of the diagram above is that its' evolution is typical for a system where r_1>1 and r_2<1. Therefore, MMA-radicals present a higher reactivity during homopropagation against TIPA-radicals. The differential equation of Mayo-Lewis [23] for copolymer composition describes the instantaneous composition (X_{MMA}) of the copolymer function of the instantaneous feed composition (x_{MMA}) and the relative reactivities. The equation shows that the two monomers are consumed at different rates. As a consequence, the feed composition continuously changes, enriching itself in the less reactive monomer.
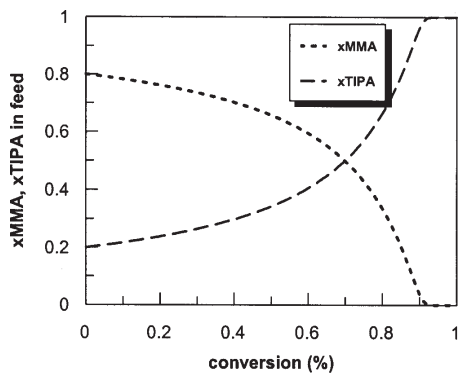
a) feed composition versus conversion
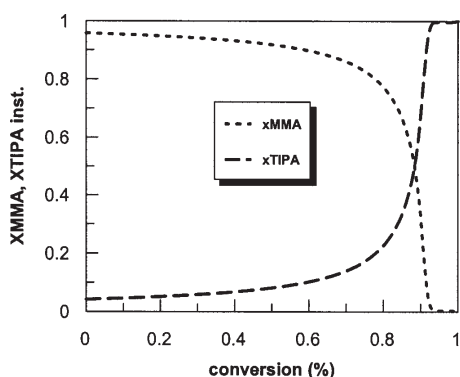
b) instantaneous copolymer composition versus conversion
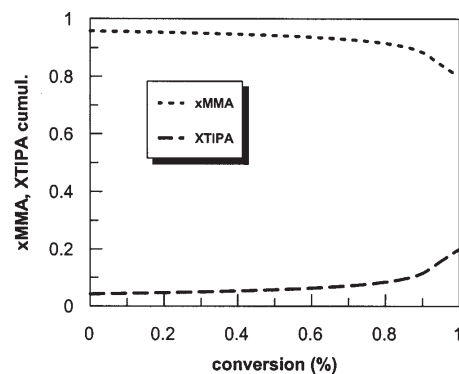
c) cumulative copolymer composition versus conversion

Fig. 4. Feed composition and copolymer compositions versus conversion (a, b, c)

In order to obtain supplementary information (the integral form of the Mayo-Lewis equation giving a correlation among composition and conversion), the average values of r_1 and r_2 are calculated in the analysed composition range, using the equation (10) [23-24].

$$\bar{r_1} = \frac{r_{21} \int_{f_1}^{f_2} \frac{r_{11}f+1}{r_{21}f+1}df}{\int_{f_1}^{f_2} df} \quad \text{and} \quad \bar{r_2} = \frac{r_{12} \int_{f_1}^{f_2} \frac{r_{22}+f}{r_{12}+f}d(\frac{1}{f})}{\int_{f_1}^{f_2} d(\frac{1}{f})} \quad (10)$$

where $f = M_1 / M_2$

The average obtained values are:

$$\bar{r_1} = 5.49,$$

$$\bar{r_2} = 0.053.$$

Integrating the Mayo-Lewis equation for the $x_{MMA} = 0.8$ and $x_{TIPA} = 0.2$ defined in the conversion interval [0..1], the following feed dependences were obtained.

The analysis of the graphics from figure 4 shows an increased reactivity of MMA-radicals towards homo-propagation, comparatively with TIPA-radicals. This
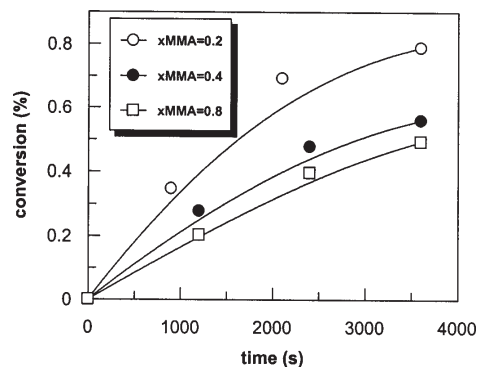

Fig. 5. Conversion versus time for the binary system MMA-TIPA
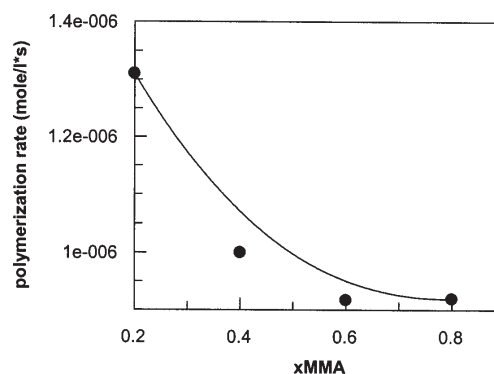

Fig. 6. Calculated copolymerisation initial rate versus feed composition

resolution is supported by the calculated values for numerical average lengths of the two sequences.

$$l_{M1} = \frac{1}{P_{12}} = \frac{1}{0.42} = 2.38$$

$$l_{M2} = \frac{1}{P_{21}} = \frac{1}{0.82} = 1.21$$

In figure 5, the evolution of the conversion versus time is presented for the analysed feeds. It is noticed a decrease of the rate as the feed enriches in MMA.

After calculating the molar composition of the obtained copolymers, initial copolymerisation rates can be also calculated (fig. 6, expressed in mole/L·s). Although MMA-radicals reactivity is obviously superior to TIPA-radicals, a decrease of initial copolymerisation rate is noticed as the feed enriches in MMA. This unusual behaviour can be due to diffusion control on the termination stage, accentuated by radical chains rigidisation due to TIPA units. Most likely, the rate-determining stage for termination is represented by segmental diffusion.

Conclusions

Different compositions of p(MMA-co-TIPA) were synthesised and physico-chemically characterised through FT-IR and elemental analysis. Reactivity ratios of the comonomers were determined. MMA reactivity is obviously superior to TIPA ($\bar{r_1} = 5.49$ and $\bar{r_2} = 0.053$), and a decrease of initial copolymerisation rate is noticed as the feed enriches in MMA.

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