COPOLYMERIZATION OF 2-[3-(2*H*-BENZOTRIAZOL-2-YL)-4-HYDROXYPHENYL]ETHYL METHACRYLATE WITH STYRENE

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Radical copolymerization of 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (M_1) with styrene (M_2) at 70 °C in 1,4-dioxane was investigated and the reactivity ratios were determined. The copolymerization was carried out as batch copolymerization to a low conversion or as copolymerization with a continuous addition of monomers at higher instantaneous conversion. The monomer reactivity ratios of the copolymerizable UV stabilizer 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate with styrene were determined using the Finemann–Ross plot for both copolymeration techniques. The estimated reactivity ratios were $r_1 = 0.588$ and $r_2 = 0.6$ for the technique of continuous addition of monomers and $r_1 = 0.462$ and $r_2 = 0.476$ and for the batch experiment. The copolymerization exhibited an azeotrope at $f_1 = 0.507$, thus a copolymer with microstructure close to the alternating one was formed at this ratio of comonomers.

Keywords: Copolymerizable UV stabilizer; Reactivity ratios; Copolymerizations; Liquid chromatography; Finemann–Ross plot; Polymers; Macromolecules; Polystyrene.

UV stabilizers are important compounds in modern paints and other polymeric materials. Their essential function is protection of binders, pigments and substrates against undesirable influence of UV radiation. Organic UV stabilizers such as benzophenone, benzotriazole, triazine, pyrimidine etc. are commonly used as additives[1]. Their drawback is usually their migration to the surface of coatings and then their easy extraction. This is the reason why the protective effect is getting down in time followed by the process of degradation of coating binders, pigments and substrates[2].

To solve the problem of UV stabilizer migration it was proposed to incorporate the UV absorbing organic compound into the polymeric chain by covalent bonds, e.g. by radical copolymerization. The group of copolymerizable UV stabilizers involves benzotriazole kind of stabilizer in the form of

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methacrylic acid ester[3]. Such a stabilizer is not extractable providing that the incorporation of stabilizer in process of copolymerization is sufficiently high. This high conversion depends on the monomer double bond reactivities, e.g. on the reactivity ratios of the comonomer couples. At present there does not exist much information on reactivity ratios of 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (**1**). The only reactivity ratios were published by Daniel Aultz, Noramco Inc. for methyl methacrylate and stabilizer[4]. The determination of reactivity ratios of 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (M_1) and styrene (M_2) is the main subject of this work. The reactivity ratios are usually determined from the copolymer composition in experiments carried out to low conversions. The other method is the determination of reactivity ratios from composition of free monomers, preferentially at high instantaneous conversion in semicontinuous copolymerization experiments[5–11]. Reactivity ratios may be evaluated by various methods, such as linear, nonlinear and other methods[12–14]. In our case, the Finemann–Ross method was used for calculation of the reactivity ratios[15].

EXPERIMENTAL

Materials

1,4-Dioxane (99.8%), tetrahydrofuran (THF), diphenyl ether (DPE), styrene (inhibitor-free), 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate, hydroquinone monomethyl ether (MEHQ), (all from Aldrich, U.S.A.), were used. Tetrahydrofuran for HPLC was dried and distilled. Diphenyl ether was used as internal standard in HPLC analysis. VAZO-52 [2,2′-azobis(2,4-dimethylpentanenitrile)] and VAZO-67 [2,2′-azobis(2-methylbutanenitrile)], (DuPont), were used as initiators. 1,4-Dioxane and styrene were purified by passing through a basic alumina column (Al_2O_3 for chromatography, type 5016A basic).

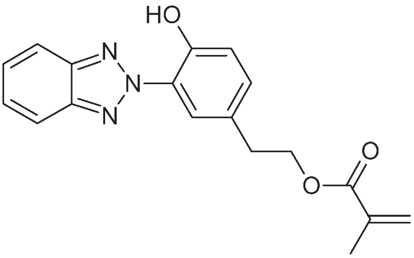

CHART 1
Structure of the used UV stabilizer

Analytical Method

HPLC was used for the determination of free monomers in the reaction mixture. The analysis was carried out using a Waters 600 pump, a Waters 717 autosampler and a Waters 996 photodiode array detector. A Nova-Pak C18 3.9 × 150 mm column was used for separation using gradient elution methanol–water (65% methanol at 0 min, 90% methanol at 15 min, 90% methanol at 20 min). 100% THF was used to flush the polymer at the end of analysis. The wavelength 270 nm was used for evaluation of the chromatograms. DPE was used as an internal standard and the peak areas of styrene and **1** were related to that of diphenyl ether. Samples were injected as 1% solutions in THF (relative to total monomers) in 5 μl of THF.

Copolymerization

The experiments were carried out either in batch to low conversions (method *A*) or as semicontinuous copolymerization at high instantaneous conversions (method *B*). Composition of copolymers was calculated from free monomer ratios in the reaction mixtures.

Method A (batch procedure): The batch procedure was carried out as a free radical copolymerization of 20 wt.% solution of monomers in 1,4-dioxane and DPE mixture at 70 °C. In each batch experiment, the exact amounts of monomers, 1,4-dioxane, DPE and VAZO 67 were charged into 5-ml glass ampoules. The concentration of DPE as an internal standard for HPLC analysis was kept constant at 50 wt.% (relative to monomers). The concentration of the VAZO 67 initiator was 1.5 wt.% relative to the monomers. The ratio of styrene and **1** in the reactions was systematically varied. The ampoules with the reaction mixture were placed into a heated oil bath for 30 min. The 30 min reaction time was selected to reach conversions below 10% so that the change of the initial monomer ratio could be neglected in the differential copolymerization equation[16]. After 30 min of copolymerization, 1000 ppm of MEHQ inhibitor (relative to monomers) as a 1,4-dioxane solution was added to each ampoule. The ampoules were placed into a refrigerator before analysis. The experiments were reproduced three times for each molar ratio.

Method B (semicontinuous procedure): The method was carried out as a the free radical copolymerization with continuous addition of 20 wt.% solution of monomers in 1,4-dioxane and DPE mixture at 70 °C under atmosphere of argon. The concentration of DPE as internal standard for HPLC analysis was kept constant at 50 wt.% relative to the monomers. The concentration of VAZO 52 initiator 1.5 wt.% relative to the monomers was used. The composition of monomer feed solution is shown in Table I.

TABLE I
Charge composition in semicontinuous copolymerization procedure. 2-[3-(2*H*-Benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (M_1) and styrene (M_2)

Charge	Component	Amount, g
A	Monomers (M_1 and M_2)	24
	1,4-Dioxane	72
	Diphenyl ether	12
B	VAZO 52 (1.5 wt.% solution in 1,4-dioxane)	12
	Total	120

The polymerization procedure was as follows: Into a 250-ml glass reactor provided with a stirrer (190 rpm), reflux condenser, thermometer and feeding device (peristaltic pump) was placed a quarter of the total amount of the reaction charge A specified in Table I and the reactor was heated in an oil bath to 70 °C. After the reaction temperature 70 °C was reached, a quarter of the initiator charge B was added to the reactor and the remaining portion, 75% of the charge B, was added to the remaining portion of a solution of the monomer mixture feed A (to keep a constant monomer/solvent ratio). Then a continuous addition of the monomer mixture and initiator solution was started. The rate of feeding solution was 0.5 ml min^{-1}, thus, the total feeding time was 3 h. The 1-ml samples for HPLC analysis were taken every 20 min. 1000 ppm of MEHQ inhibitor (relative to monomers) as a 1,4-dioxane solution were added to each sample and kept in refrigerator before analysis.

RESULTS AND DISCUSSION

The experiments were carried out in 1,4-dioxane. The reason for choosing this solvent was a very limited solubility of the copolymerizable UV stabilizer (M_1) in almost every solvent. We evaluated 1,4-dioxane and tetrahydrofuran as the best solvent as they were able to dissolve the monomer mixtures in any molar ratio even at 25 °C giving total solution concentrations up to 20 wt.%. 1,4-Dioxane was used preferentially due to its higher boiling point. As the common gas chromatography could not be used for the free monomer analysis due to thermal degradation of **1**, HPLC with a UV detector was used. DPE was chosen as an internal standard for free monomer determination. DPE was suitable as a co-solvent, since it does not affect the copolymerization and its absorbance is slightly lower than those of monomers. The wavelength 270 nm was used for the determination as the absorbances of DPE and both the monomers were found to be close to each other in this region (Fig. 1). The constant concentration of DPE during the copolymerization enabled easy calculation of conversion of both monomers. The monomer conversion C was calculated from peak areas at the beginning of the reaction A_0 and peak areas after a polymerization time A_t that were related to the diphenyl ether area A_{DPE}:

$$C = (A_0/A_{\text{DPE}} - A_t/A_{\text{DPE}})/(A_0/A_{\text{DPE}}) \,. \qquad (1)$$

Method A

The data obtained from free monomer analysis for batch copolymerization are summarized in Table II.

It can be shown that the conversion for both monomers in most experiments did not exceed 10%. The obtained values of monomer ratios in the

TABLE II
Initial and final mole fractions (f_1, f_2 and F_1, F_2) of free monomers in the batch copolymerization. 2-[3-(2*H*-Benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (M_1) and styrene (M_2)

Run	Initial mole fractions of monomers		Conversion %	Calculated mole fractions of monomers in copolymers	
	M_1, f_1	M_2, f_2		M_1, F_1	M_2, F_2
1	0.142	0.858	15.1	0.223	0.777
2	0.258	0.742	9.5	0.333	0.667
3	0.336	0.664	9.6	0.385	0.615
4	0.437	0.563	10.3	0.455	0.543
5	0.51	0.492	9.5	0.513	0.487
6	0.571	0.429	14.4	0.569	0.431
7	0.627	0.372	9.2	0.658	0.342
8	0.674	0.326	6.9	0.633	0.367
9	0.718	0.282	2.9	0.664	0.336
10	0.756	0.243	7.6	0.695	0.305
11	0.792	0.208	6.3	0.686	0.314
12	0.823	0.177	5.2	0.739	0.261
13	0.853	0.147	5.5	0.764	0.236
14	0.879	0.121	8.3	0.814	0.186
15	0.903	0.097	5.4	0.837	0.163
16	0.926	0.075	7.5	0.871	0.129

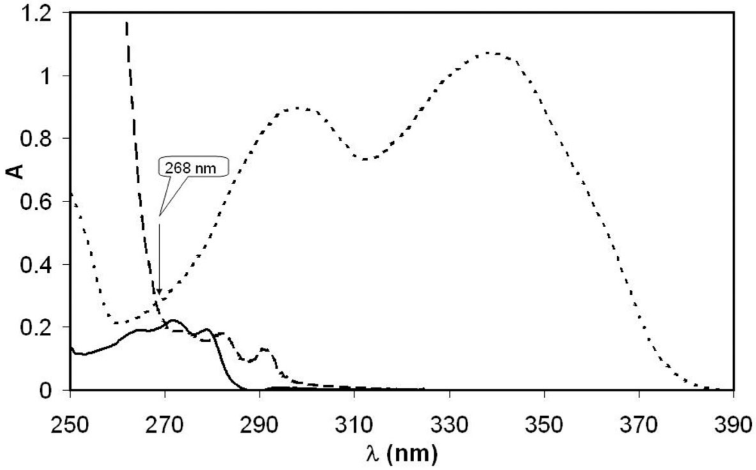

FIG. 1
Ultraviolet spectra in 1,4-dioxane at concentration 20 mg l^{-1}. – – – Styrene, - - - 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate and —— diphenyl ether

free monomer mixture and in the copolymer were used for calculation of reactivity ratios using the Finemann-Ross plot. According to this method, the monomer reactivity ratios can be obtained from the equation[17]:

$$Y = Xr_1 - r_2 \qquad (2)$$

the reactivity ratios, r_1 and r_2, correspond to the M_1 and M_2 monomers, respectively. The parameters X and Y are defined as follows:

$$X = a^2/b \quad \text{and} \quad Y = a - a/b \qquad (3)$$

with

$$a = f_1/(1 - f_1) \quad \text{and} \quad b = F_1/(1 - F_1) \qquad (4)$$

where f_1 is the mole fraction of monomer M_1 at the beginning of the copolymerization and F_1 is the mole fraction of monomer M_1 in copolymer that was calculated from the free monomer ratio at the end of copolymerization to a required conversion. The used data are summarized in Table III.

TABLE III
Determination of reactivity ratios according to Finemann and Ross (F–R), batch experiments – method *A* (see Eqs (*3*) and (*4*))

Run	*a*	*b*	F–R		Reciprocal F–R	
			Y	*X*	Y_R	X_R
1	0.7771	0.8335	–0.1552	0.7246	–0.2142	1.3801
2	1.0379	1.0532	0.0524	1.0228	0.0512	0.9777
3	1.3329	1.3215	0.3243	1.3443	0.2412	0.7440
4	1.6849	1.9210	0.8080	1.4778	0.5466	0.6767
5	2.0714	1.7225	0.8689	2.4909	0.3488	0.4014
6	2.5459	1.9781	1.2589	3.2766	0.3842	0.3052
7	3.1066	2.2751	1.7412	4.2420	0.4105	0.2357
8	3.8023	2.1831	2.0606	6.6223	0.3112	0.1510
9	4.6577	2.8293	3.0114	7.6677	0.3927	0.1304
10	5.7874	3.2390	4.0006	10.3409	0.3869	0.0967
11	7.2517	4.3750	5.5941	12.0200	0.4654	0.0832
12	9.3244	5.1412	7.5108	16.9111	0.4441	0.0591
13	12.4230	6.7431	10.5806	22.8869	0.4623	0.0437
14	0.1659	0.2865	–0.4131	0.0961	–4.3006	10.4103
15	0.3474	0.4986	–0.3494	0.2421	–1.4432	4.1308
16	0.5054	0.6270	–0.3007	0.4074	–0.7380	2.4546

Note: $a = m_1/m_2$, $b = M_1/M_2$; $Y = a - a/b$, $X = a^2/b$; $Y_R = b - 1/a$, $X_R = b/a^2$.

Reactivity ratios for copolymerization of 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate and styrene were found to be r_1 = 0.475 and r_2 = 0.462 (r_1r_2 = 0.22) with an azeotrope of $f_{(\mathrm{Sty})}$ = 0.507.

Method B

Another method for a semicontinuous process with continuous addition of monomers in a given ratio to the copolymerizing system was used for the determination of reactivity ratios. In the initial period of the monomer mixture feeding, the result copolymer is richer in the more reactive comonomer. Therefore, the monomer mixture is enriched by the less reactive monomer until the monomer ratio in the reactor produces the copolymer of composition equal to the monomer ratio in the monomer feed. The data obtained by the monomer analysis for copolymerization with a continuous addition of monomers at high instantaneous conversion are summarized in Table IV.

TABLE IV
Equilibrium composition of free monomers in the reaction mixture during the feeding of the monomer mixture (f_1, f_2) and the instantaneous copolymer composition (F_1, F_2) that is equal to the composition of monomer mixture feed in semicontinuous procedure – method *B*. 2-[3-(2*H*-Benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (M_1) and styrene (M_2)

Run	Analyzed free monomer composition in the reaction mixture at the steady state (mole fraction)		Copolymer composition equal to the monomer feed composition (mole fraction)	
	M_1, f_1	M_2, f_2	M_1, F_1	M_2, F_2
1	0.220	0.780	0.166	0.834
2	0.385	0.615	0.331	0.669
3	0.455	0.545	0.437	0.563
4	0.746	0.254	0.791	0.209
5	0.531	0.469	0.509	0.491
6	0.566	0.434	0.573	0.427
7	0.609	0.394	0.627	0.373
8	0.656	0.344	0.674	0.326
9	0.702	0.298	0.756	0.244
10	0.746	0.254	0.791	0.209
11	0.805	0.195	0.852	0.148
12	0.862	0.138	0.903	0.097

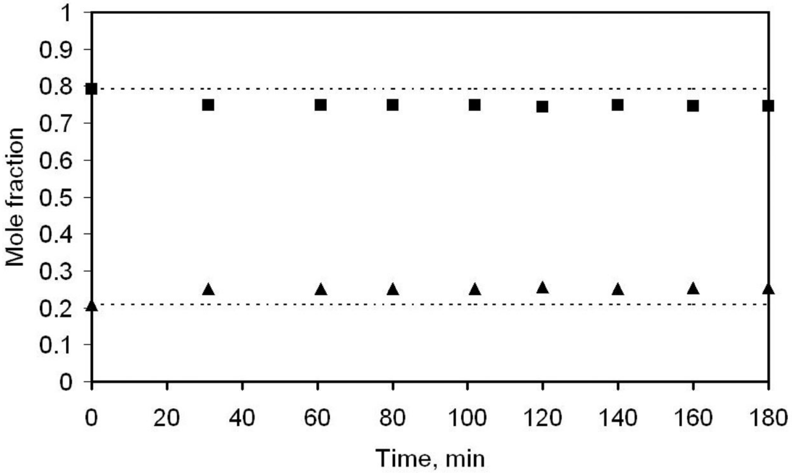

FIG. 2

Mole fractions of free monomers and the reaching the equilibrium composition, ratio of monomers in the monomer emulsion feed [Sty/**1**] = 0.791/0.209. ■ Styrene and ▲ 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (see Table IV)

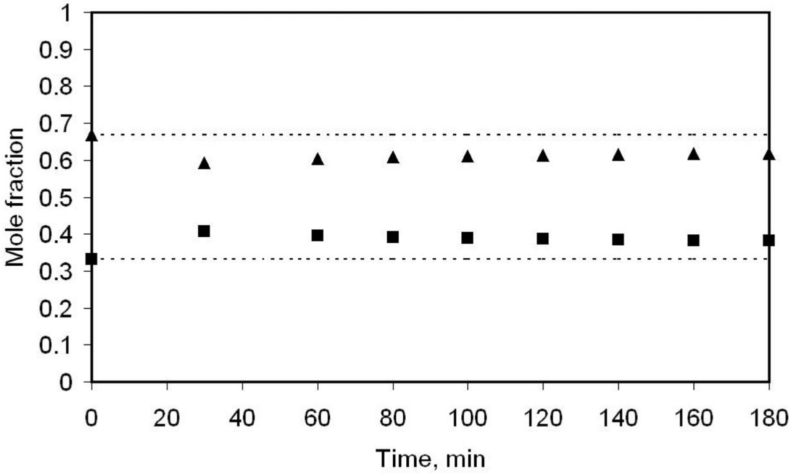

FIG. 3

Mole fractions of free monomers and the reaching the equilibrium composition, ratio of monomers in the monomer emulsion feed [Sty/**1**] = 0.331/0.669. ■ Styrene and ▲ 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (see Table IV)

TABLE V
Determination of reactivity ratios, semicontinuous procedures – method *B* (see Eqs (*3*) and (*4*))

Run	a	b	F–R		Reciprocal F–R	
			Y	X	Y_R	X_R
1	1.0349	1.1311	0.1199	0.9469	0.1266	1.0561
2	1.3416	1.3052	0.3137	1.3790	0.2275	0.7251
3	1.6784	1.5373	0.5866	1.8323	0.3201	0.5457
4	2.0707	1.9073	0.9850	2.2481	0.4381	0.4448
5	3.1050	2.3545	1.7860	4.0939	0.4363	0.2443
6	3.7918	2.9648	2.5128	4.8495	0.5182	0.2062
7	5.7699	4.1158	4.3680	8.0887	0.5400	0.1236
8	9.3128	6.2349	7.8191	13.9100	0.5621	0.0719
9	0.1982	0.2824	–0.5034	0.1390	–3.6209	7.1922
10	0.4939	0.6270	–0.2938	0.3891	–0.7552	2.5701
11	0.7761	0.8336	–0.1550	0.7227	–0.2144	1.3836

Note: $a = m_1/m_2$, $b = \mathrm{M}_1/\mathrm{M}_2$; $Y = a - a/b$, $X = a^2/b$; $Y_R = b - 1/a$, $X_R = b/a^2$.

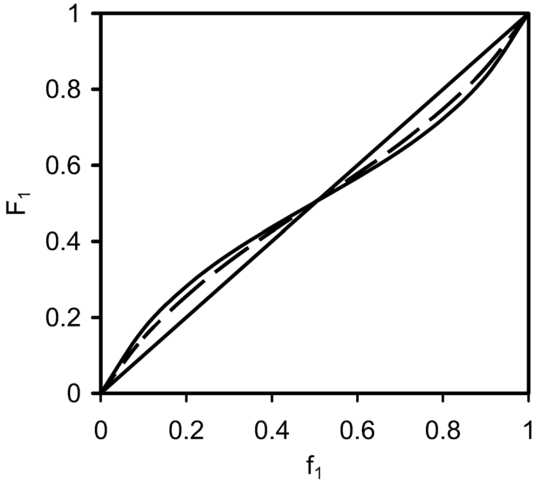

FIG. 4
Copolymerization diagram of 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate (M_1) and styrene (M_2). Data obtained by —— method *A* and – – – method *B*

In this semicontinuous procedure the copolymer composition was equal to the monomer composition after the steady state was reached. The rate of monomer mixture addition was sufficiently low so that the steady free monomer composition was reached in all investigated monomer ratios. The examples for the monomer emulsion feed ratios styrene/**1** = 0.791/0.209 and styrene/**1** = 0.331/0.669 are shown in Figs 2 and 3.

The reactivity ratios were determined similarly as in the batch copolymerization (method *A*). The experimental data for the feed and copolymer composition are summarized in Table IV. The data that were used for determination of reactivity ratios are shown in Table V. The reactivity ratios were determined from the Finemann–Ross plot.

The reactivity ratios for copolymerization of 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate and styrene are found to be $r_1 = 0.6$ and $r_2 = 0.588$ ($r_1 r_2 = 0.3528$) with an azeotrope of $f_{(\mathrm{Sty})} = 0.509$. The found values were close to those determined from free monomers in the batch copolymerization. The copolymerization diagrams are shown in Fig. 4.

CONCLUSION

The copolymerization of styrene and 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate was investigated by two free radical copolymerization techniques in 1,4-dioxane at 70 °C. The reactivity ratios were determined by the linear method of Finemann and Ross. The reactivity ratios for batch copolymerization were found to be $r_1 = 0.475$ and $r_2 = 0.462$ with an azeotrope of $f_{(\mathrm{Sty})} = 0.507$. The reactivity ratios for semicontinuous procedure were found to be $r_1 = 0.6$ and $r_2 = 0.588$ with an azeotrope of $f_{(\mathrm{Sty})} = 0.509$. The found reactivity ratios indicate that 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate is incorporated randomly into the polymer chain and there is a tendency to alternation when the monomer composition is close to the azeotropic point. Small differences found between the reactivity ratios determined by methods *A* and *B* were apparently caused by a use of different copolymerization techniques. The experimental results indicate that 2-[3-(2*H*-benzotriazol-2-yl)-4-hydroxyphenyl]ethyl methacrylate easily copolymerizes with styrene in real systems, in which it is used in relatively low concentrations.

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