

Instituto de Plásticos y Caucho  
Juan de la Cierva, 3, Madrid-6, Spain

## **Reactivity of Vinyl Ketones in Free Radical Copolymerization with Methyl Methacrylate and Vinyl Acetate**

Roberto Sastre, José L. Acosta, Rosario Garrido, and José Fontán

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### **SUMMARY:**

The reactivity of some monomer vinyl ketones in the radical copolymerization with methyl methacrylate and vinyl acetate was studied on the basis of the Taft equation. It was concluded that the relative reactivities of the vinyl ketones in radical reactions increase with increasing electron-withdrawing nature of the vinyl ketone substituent. Polar and steric effects do not affect the reactivity.

### **ZUSAMMENFASSUNG:**

Die Reaktivität verschiedener monomerer Vinylketone bei der radikalischen Copolymerisation mit Methylmethacrylat und Vinylacetat wurden auf der Basis der Taft-Gleichung untersucht. Es ergab sich, daß die relative Reaktivität der Vinylketonmonomeren mit zunehmender Elektronegativität der Substituenten der verschiedenen Vinylketone steigt. Polare und sterische Effekte beeinflussen die Reaktivität nicht.

### *Introduction*

In order to describe new controlled photodegradable materials, we have reported in previous papers<sup>1</sup> the kinetics of the free radical copolymerization of acrylonitrile with several vinyl ketones. In the present one, the reactivity and kinetics of the same vinyl ketones in the free radical copolymerization with methyl methacrylate and vinyl acetate are described.

### *Experimental*

*t*-Butyl vinyl ketone (TBVK), phenyl vinyl ketone (PVK), isopropyl vinyl ketone (IPVK) and ethyl vinyl ketone (EVK) were obtained by heating the appropriate acyl chloride in methylene chloride solutions with ethylene and aluminium chloride<sup>2</sup>.

Tab. 1. Copolymerization of Methyl Methacrylate ( $M_1$ )-Vinyl Ketones ( $M_2$ ) in Benzene<sup>a</sup>.

MMA/VK <sup>b</sup>	t-Butyl vinyl ketone yield (%)	$F_2^c$	Phenyl vinyl ketone yield (%)	$F_2^c$	Ethyl vinyl ketone yield (%)	$F_2^c$	Isopropyl vinyl ketone yield (%)	$F_2^c$
10/0	5,23	0,0000	5,23	0,0000	5,23	0,0000	5,23	0,0000
9/1	3,30	0,0798	3,42	0,1280	5,52	0,2214	11,20	0,1395
7/3	5,21	0,2506	22,86	0,2486	5,02	0,3334	3,10	0,3973
5/5	8,92	0,4389	7,22	0,5853	9,91	0,5278	10,0	0,4817
3/7	9,13	0,6465	3,42	0,6386	6,28	0,6853	7,21	0,8285
1/9	14,93	0,8517	—	—	5,28	0,8798	7,91	0,8643
0/10	7,19	1,0000	7,19	1,0000	7,19	1,0000	7,19	1,0000

<sup>a</sup> Temp. = 60°C,  $[M_1] + [M_2] = 7$  mol/l;  $[AIBN] = 0,0204$  mol/l.<sup>b</sup> Volume ratio of monomers.<sup>c</sup>  $F_2$  is the mol fraction of vinyl ketones in copolymers.

Tab. 2. Copolymerization of Vinyl Acetate ( $M_1$ ) with Vinyl Ketones ( $M_2$ ) in Benzene<sup>a</sup>.

VA/VK <sup>b</sup>	t-Butyl vinyl ketone yield (%)	$F_2^c$	Phenyl vinyl ketone yield (%)	$F_2^c$	Ethyl vinyl ketone yield (%)	$F_2^c$	Isopropyl vinyl ketone yield (%)	$F_2^c$
8/0	7,18	0,0000	7,18	0,0000	7,18	0,0000	7,18	0,0000
6/2	9,7	0,8163	4,30	0,7778	19,18	0,8574	19,71	0,8600
5/3	7,8	0,7118	2,27	0,8355	16,77	0,8905	11,79	0,8722
4/4	9,2	0,5972	6,90	0,8608	12,18	0,9702	8,77	0,9021
3/5	11,2	0,4895	5,70	0,9221	17,40	0,9556	15,34	0,9540
2/6	12,8	0,3483	7,16	0,9474	15,85	0,9616	10,33	0,9500
1/8	9,50	1,0000	9,50	1,0000	9,50	1,0000	9,50	1,0000

<sup>a</sup> Temp. = 60°C,  $[M_1] + [M_2] = 7 \text{ mol/l}$ ;  $[AIBN] = 0,0204 \text{ mol/l}$ .<sup>b</sup> Volume ratio of monomers.<sup>c</sup>  $F_2$  is the mol fraction of vinyl ketones in copolymers.

Methyl methacrylate (MMA) was washed with dilute sodium hydroxide aqueous solution, then with water to neutrality, and finally dried over anhydrous sodium sulphate. It was then distilled under nitrogen. Vinyl acetate (VAc) was purified by a method similar to that described by Mathenson et al.<sup>3</sup>. Benzene was purified by fractionated distillation from the commercial product. Azobisisobutyronitrile (AIBN) was recrystallized twice from chloroform by addition of methanol, and dried under vacuum at 20°C.

The copolymers were prepared by free radical polymerization in sealed tubes under vacuum using benzene as solvent and AIBN as initiator. The polymers were reprecipitated several times with methanol to remove catalyst residues and unreacted monomer, then dried in the dark up to constant weight under vacuum and light protection.

The composition of the copolymers was determined from their elementary analysis and by NMR analysis<sup>4</sup>; NMR spectra were recorded on a Perkin-Elmer R-12, working at 60 MHz in CDCl<sub>3</sub> solution at 30°C by using tetramethylsilane as an internal standard. The vinyl acetate content was also calculated according to the method of Aydin<sup>5</sup>. The intrinsic viscosities were determined at 30°C from solutions in benzene using an Ubbelohde viscometer.

Reactivity ratios of the monomers were calculated from the copolymer composition using the Fineman-Ross method<sup>6</sup> and the Q-e parameters were determined according to the Alfrey-Price scheme<sup>7</sup>.

### *Results and Discussion*

The conditions and results of the radical copolymerization in benzene solutions of methyl methacrylate or vinyl acetate and the several vinyl-ketone monomers at 60°C are summarized in Tab. 1 and 2.

The behaviour of the copolymerization reactions, which is the purpose of the present work, is similar in some way to that observed in the copolymerization of vinyl ketones with acrylonitrile, described in the first part of this series<sup>1</sup>. The reactivity of the vinyl ketones studied in the copolymerization with methyl methacrylate and vinyl acetate has been calculated on the basis of the effect on their substituents, applying the Taft equation,

$$\log 1/r_1 = \rho^* \sigma^* + \delta E_s \quad (1)$$

where  $\sigma^*$  and  $E_s$  are polar and steric substituent constants, and  $\delta$  and  $\rho^*$  are reaction constants.

From the values in Tab. 1 and 2, the copolymerization reactivity ratios for vinyl ketones and methyl methacrylate or vinyl acetate were calculated and are summarized in Tab. 3 and 4 respectively. As can be seen from these tables, all the vinyl ketones were more reactive towards methyl methacrylate than towards vinyl acetate.

*Copolymerization of vinyl ketones*

Tab. 3. Copolymerization Reactivity Ratios of Vinyl Ketones ( $M_2$ ) in Free Radical Copolymerization with Methyl Methacrylate ( $M_1$ ) at 60°C.

$R^a$	$f_1$	$r_2$	$\log(1/r_1)$	$Q_2$	$e_2$	$\sigma^*$ of $R^b$
$C_2H_5$	0,79	0,79	0,0985	0,53	0,42	-0,10
$i-C_3H_7$	0,81	1,44	0,0899	0,79	0,60	-0,13
$t-C_4H_9$	0,80	1,20	0,0969	0,94	1,20	-0,30
$C_6H_5$	0,64	1,97	0,1938	0,96	0,14	0,60

<sup>a</sup> Aliphatic or aromatic rest in vinyl ketone.

<sup>b</sup> Reference<sup>10</sup>.

Tab. 4. Copolymerization Reactivity Ratios of Vinyl Ketones ( $M_2$ ) in Free Radical Copolymerization with Vinyl Acetate ( $M_1$ ) at 60°C.

$R^a$	$r_1$	$r_2$	$\log(1/r_1)$	$Q_2$	$e_2$	$\sigma^*$ of $R^b$
$C_2H_5$	0,13	8,68	0,886	0,53	0,42	-0,10
$i-C_3H_7$	0,3	7,87	0,886	0,79	0,60	-0,13
$t-C_4H_9$	0,15	7,00	0,824	0,94	1,20	-0,30
$C_6H_5$	0,10	6,5	1,000	0,96	0,14	0,60

<sup>a</sup> Aliphatic or aromatic rest in vinyl ketone.

<sup>b</sup> Reference<sup>10</sup>.

In order to evaluate the structural effect of the aromatic and aliphatic substituents of the vinyl ketones with respect to the copolymerizations, the relative reactivities  $\log(1/r_1)$  of the vinyl ketones towards the polymethyl methacrylate or polyvinyl acetate radical were plotted against the  $\sigma^*$  constants of the alkyl or aryl groups of the vinyl ketones. The results are shown in Fig. 1.

This figure shows fairly good straight relationships in both cases suggesting that an increase in the reactivity of the vinyl ketones is due to an increase in the electron-attracting force of their aliphatic or aromatic substituent. From the slopes of the straight lines in Fig. 1  $\rho^*$  values were obtained; a value of 0,14 was calculated for  $\rho^*$  in vinyl ketone-methyl methacrylate copolymers and a value of 0,21 for  $\rho^*$  in vinyl ketone-vinyl acetate copolymers. When  $[\log(1/r_1) - \rho^*\sigma^*]$  was plotted against  $E_s$  (see Eq. 1) a straight line with  $\delta=0$  was obtained. The fact that the resulting  $\delta$  value in Eq. (1) was

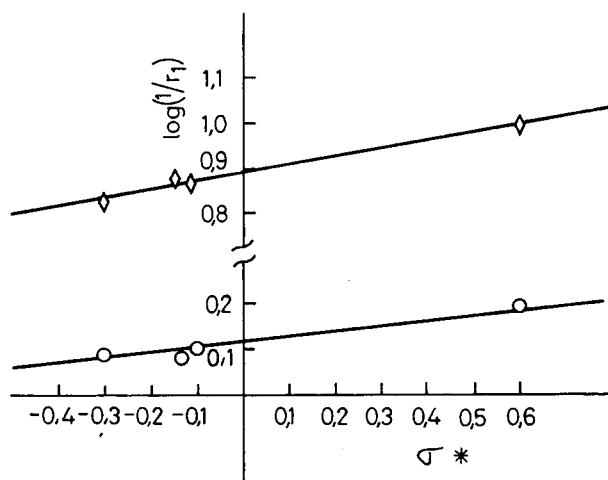


Fig. 1. Plots of  $\log(1/r_1)$  versus hammet  $\sigma^*$  constants of R-groups in vinyl ketone, in copolymerization with methyl methacrylate ( $\circ$ ) and with vinyl acetate ( $\diamond$ ).

zero in both cases, is the same as that observed for acrylonitrile-vinyl ketone copolymerization reactions<sup>1</sup>, indicating that the reactivities of vinyl ketones do not depend on the steric requirement of their aliphatic or aromatic substituents. From all these values, it was concluded that the relative reactivities of the vinyl ketones in radical reactions increase with increasing electron-withdrawing nature of the vinyl ketone substituent. Polar and steric effects do not seem to affect the reactivity.

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