TEMPLATE PHOTOPOLYMERIZATION OF METHACRYLIC ACID—III. DETERMINATION OF THE RATE CONSTANTS RATIO k_t/k_p FOR ELEMENTARY PROCESSES

Jadwiga Matuszewska-Czerwik and Stefan Połowiński*

Institute of Synthetic Fibres, Technical University of Łódź, 90-924 Łódź, Żwirki 36, Poland

Abstract—Polymerization of methacrylic acid (MAA) in aqueous system in the presence of templates (poly *N*-vinyl-2-pyrolidone, polyethylene glycol, polyethylene glycol with azo groups) was investigated with UO_2SO_4 as photoinitiator. The overall rate constants were found. The post-effect polymerization after switching off the lamp was examined and the ratio k_t/k_p was found. Using the rotating sector method, the life-time of macroradicals for polymerization without template was determined and k_t/k_p was calculated. The post-effect polymerization for MAA with templates and without photoinitiator was investigated and k_t/k_p was calculated. The influences of various templates on the photopolymerization and on the post-effect are discussed.

INTRODUCTION

One of the major factors affecting template polymerization is the template–monomer interaction and this problem has been dealt with in our studies on the photopolymerization of methacrylic acid (MAA) in aqueous systems in the presence of various templates [1, 2] as well as in the work of other authors on template polymerization of this monomer in various systems [3–10].

In order to gain more knowledge about the template polymerization, it is essential to study the rate of elementary processes. Only two papers have dealt with the determination of rate constants in template polymerization, by the rotating sector method [9] and by a calorimetric method [10].

It was shown [2] that the ratio of the rate constant of termination to that of propagation (k_t/k_p) can be determined by examination of the template polymerization proceding after cutting off the light source in the so-called post-effect. The derived equation allows finding the ratio graphically. In previous studies, $Na_2S_2O_8$ was used as photoinitiator. At 25°, thermal polymerization of MAA takes place to a small extent because of decomposition of $Na_2S_2O_8$. As had been shown [12], the polymerization has insignificant effect on the rate of the template photopolymerization. The overall rate constant, pseudo first order with respect to monomer, is $2.2 \times 10^{-5}\,sec^{-1}$ for the thermal polymerization and $4.4 \times 10^{-4}\,sec^{-1}$ for the template photopolymerization of MAA in the presence of PVP under the same conditions. The influence of the thermal polymerization in the post-effect is also insignificant. The thermal polymerization however should be taken into account in non-template polymerization when using the rotating sector method to determine the life-time of macroradicals. The life-time and k_t/k_p for the

non-template polymerization given in Table 1 have been determined with the thermal polymerization being taken into account. In the present study, we have used UO_2SO_4 as photoinitiator which, according to the literature on photopolymerization of MAA [13], does not bring about thermal polymerization, as confirmed experimentally by us. Using the rotating sector method, we found the radical life-time in the polymerization without template. In the template polymerization, the ratio k_t/k_p was determined from the course of post-effect. This paper includes also the results for the post-effect in polymerization initiated with the template itself [14] and k_t/k_p calculated by the method given previously.

EXPERIMENTAL PROCEDURES

1. Reagents

MAA and water were prepared as described previously [1]. The templates, poly(vinylpyrolidone) (PVP) ($\bar{P}_v = 8660$), polyethylene glycol (PEG_{20000}) ($\bar{P}_v = 454$), (PEG_{6000}) ($\bar{P}_v = 136$), polyethylene glycol with azo groups (PEGN) ($\bar{P}_v = 91$) and photoinitiator were used without additional purification.

2. Apparatus

Polymerization was carried out in a quartz dilatometer in a water thermostat provided with a quartz window. A xenon tube, type XBO150 W/1, set 40 cm from the dilatometer, was the light source. Calculations of the conversion were made as described previously [1].

3. Photopolymerization

In all the MAA photopolymerizations in water, without and with template, the same concentrations were used, viz. [MAA] = 0.1 mol/l; $[UO_2SO_4] = 1.8 \times 10^{-3}$ mol/l with the ratio (monomer unit) to (template unit) = 1. The photopolymerization without template and the effects of all the templates on the photopolymerization were examined (Fig. 1) at 25°. It was found that at low conversions all the photopolymerizations were first order with respect to monomer.

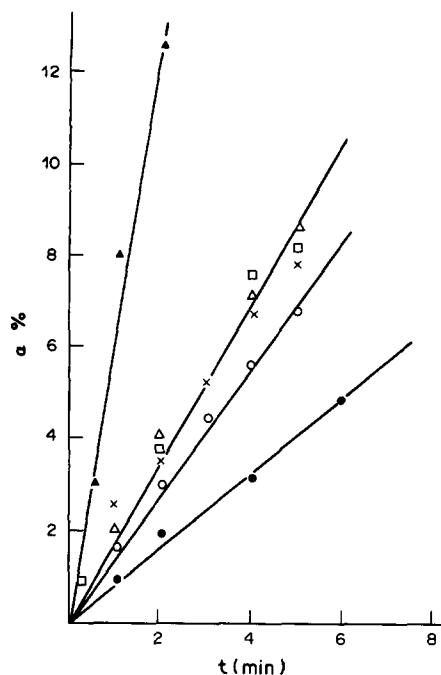*To whom all correspondence should be addressed.

Fig. 1. Influence of templates on the polymerization of MAA with UO_2SO_4 as initiator. Conversion vs time. $\bigcirc$, Blank polymerization; $\square$, with PEG_{20000}; $\triangle$, with PEGN; $\times$, with PEG_{6000}; $\blacktriangle$, with PVP for comparison; $\bullet$, with $Na_2S_2O_8$ without template.

4. Determination of the radical life-time

Using the rotating sector method [16], the reaction rate was measured in the non-stationary state of the system $(MAA + UO_2SO_4)$ without template. Flash times were within the range 1–100 sec. The ratio of darkness time to flash time "r" was 3. The life-time of MAA macroradicals "τ" in an aqueous system determined under these conditions is 1.42 sec (Fig. 2).

Using the relationship

$$\frac{k_p}{k_t} = \frac{2 \cdot \tau \cdot v_c}{[M]} \quad [11]$$

where V_c = polymerization rate with continuous illumination; [M] = initial monomer concentration, k_t/k_p was calculated (see Table 1).
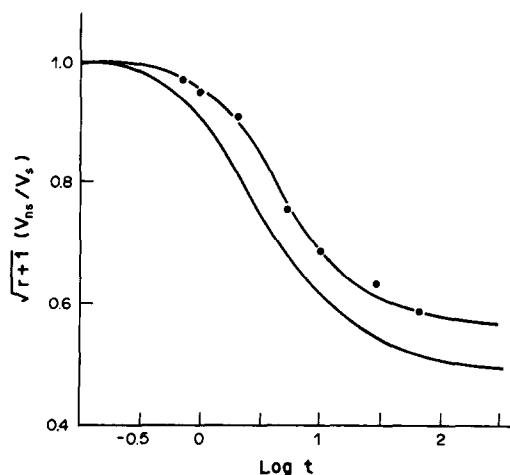

Fig. 2. Rotating sector curve for polymerization of MAA with UO_2SO_4 as photoinitiator.

Table 1. Overall rate constants, k_t/k_p, and life-time for template polymerization of MAA with various initiators and templates

Initiator	Template	k (sec^{-1})	k_t/k_p	τ (sec)
UO_2SO_4	—	2.4×10^{-4}	1510	1.42
UO_2SO_4	GPEN	2.9×10^{-4}		
UO_2SO_4	GPE_{6000}	2.9×10^{-4}		
UO_2SO_4	GPE_{20000}	2.9×10^{-4}	8.6	
UO_2SO_4	PVP	6.7×10^{-4}	8.3	
$Na_2S_2O_8$	—	1.55×10^{-4}	1250	3.52
$Na_2S_2O_8$	PVP	4.4×10^{-4}	16.9	
—	GPE_{20000}	3.3×10^{-5}	38	
—	GPEN	5.6×10^{-5}	38	
—	PVP	8.6×10^{-5}	11.5	

5. Examination of the post-effect polymerization

The course of polymerization after turning off the light was examined in all the systems under investigation: $(MAA + UO_2SO_4)$ (Fig. 3); $(MAA + UO_2SO_4 +$ each template) (Figs 4 and 5) and (MAA + each template) (Figs 6 and 7).

All the photopolymerizations were continued for 5 min to allow the radical concentration to become steady and then the illumination was interrupted.

Based on the relationship derived previously [2]:

$$\frac{1-\alpha}{\dfrac{d\alpha}{dt}} = \frac{k_t}{k_p} \cdot t + \text{const.}$$

the values of k_t/k_p were found graphically and are shown in Table 1.

Figure 8 shows an example of the relationship

$$\frac{1-\alpha}{\dfrac{d\alpha}{dt}} = f(t)$$

for the system $(MAA + UO_2SO_4 + PVP)$.

RESULTS AND DISCUSSION

Figure 1 shows that UO_2SO_4 is a much more effective photoinitiator than $Na_2S_2O_8$ previously used, as indicated by the increase in the overall rate constant from 1.55 to 2.4 sec^{-1}. (Table 1). It appears from Fig. 3 that, after cutting off the illumination in the absence of template, there is an immediate break in polymerization. One may be certain that no further thermal polymerization takes place. The effect of templates on the polymerization rate is illustrated in Fig. 1; the templates PEG_{20000}, PEG_{6000} and PEGN

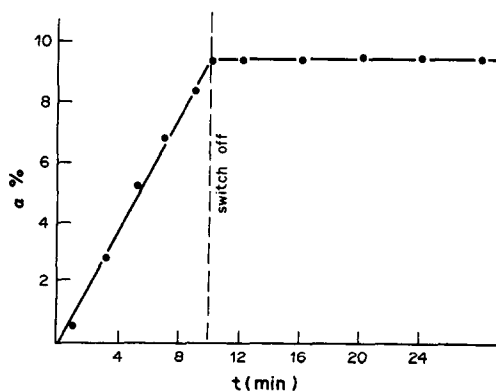

Fig. 3. Conversion in the post-effect for polymerization of MAA with UO_2SO_4 as initiator without template.

have rather small effects on the rate. On the other hand the PVP template brings about clear increase in the rate. The overall rate constant increases more than three times (Table 1). Similar effect of the PVP template was observed in the MAA photopolymerization in the presence of $Na_2S_2O_8$ as initiator [2].

In order to find the value of k_t/k_p in the polymerization without template, measurements of the radical life-time were made by the rotating sector method, using UO_2SO_4 as photoinitiator. Previously the radical life-time was determined using $Na_2S_2O_8$ as initiator, with suitable corrections for thermal polymerization [12]. The values of τ and the values of k_t/k_p calculated from them are listed in Table 1.

For MAA polymerization in aqueous system without template [14], values of k_t/k_p were determined at 6.5–22°. To compare our results for 25° with those in the literature, the latter were extrapolated to 25°. The value of k_t/k_p obtained from the extrapolation is 2380, i.e. almost twice our value, but a different experimental procedure was used [14] and also a different initiator and extrapolation has been used. The order of magnitude of k_t/k_p in both cases is the same.

In order to consider the mechanism of the template polymerization, we compare the kinetic results for the polymerization without template with those for the template polymerization. The values of k_t/k_p with template were determined on the basis of the polymerization course in the post-effect according to the procedure described previously [2]. The results are listed in Table 1.

The values of k_t/k_p in the template polymerization are more than two orders of magnitude smaller than those in the polymerization without template. Lower values of k_t/k_p in template polymerizations have been reported but they refer to polymerization in non-aqueous systems. Thus, for MAA polymerization on PMAA in DMF at 5° [11] the value of k_t/k_p was lower by one order of magnitude than in the polymerization without template. A lowering by three orders of magnitude was found for MAA polymerization on polyvinylpyrrolidone in DMF at 30° [10].

This result confirms the suggestion that the termination constant in template polymerization is considerably reduced, while the propagation constant is only slightly decreased [10]. The macroradicals combined with template show considerably lower mobility and lower tendency to recombine as compared with analogous reactions during the polymerization without template. This difference probably accounts for the decrease in k_t.
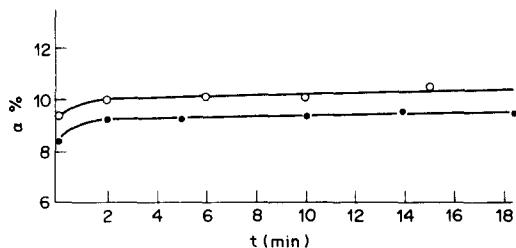

Fig. 4. Conversion in the post-effect for polymerization of MAA with UO_2SO_4 as initiator and with templates: O, PEG_{6000}, ●, PEGN.
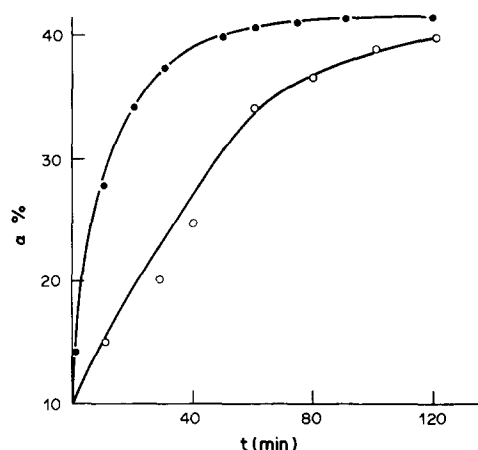

Fig. 5. Conversion in the post-effect for MAA with UO_2SO_4 for templates: ●, PVP; O, PEG_{20000}.

Investigating the polymerization of MAA in the post-effect in the presence of various templates showed that the effect of template depends on the molecular weight. For instance, PEG_{20000} (DP = 454) brings about polymerization in post-effect, (Fig. 5), while PEG_{6000} (DP = 136) and PEGN (DP = 91) do not, (Fig. 4).

It is note-worthy that k_t/k_p calculated for the polymerization in the presence of PEG_{20000} is much the same as that for the PVP template polymerization (Table 1). On the other hand, the low molecular templates having no effect on photopolymerization, do not bring about polymerization in the post-effect. It may be assumed that the template behaviour in the photopolymerization is different from that in the post-effect. This view is confirmed by the fact that PEG_{20000} does not accelerate the photopolymerization but brings about polymerization in post-effect. On the other hand, PVP clearly accelerates the photopolymerization (Fig. 1) and brings about polymerization in post-effect (Fig. 5). The role of template in the post-effect consists in bonding the previously formed radicals and consequently reducing their mobility. The effect of the polyethylene glycol template on MAA is very small and therefore the photopolymerization rate is not affected. However, during photopolymerization, complexes of macroradicals and polyethylene glycol are formed. In the post-effect, the macroradicals are already combined with the template, so reducing their mobility and consequently lowering k_t.

It seems that a template with low molecular weight does not reduce the mobility of macroradical significantly and the termination takes place very rapidly, and therefore in such cases no polymerization is observed in the post-effect.

This paper contains also the results of studies on the polymerization in post-effects, photopolymerization taking place in the presence of templates which themselves act as photoinitiators as described previously [15]. Figures 6 and 7 show the course of polymerization in the post-effect. k_t/k_p has been calculated as previously and the values are given in Table 1. The value of 11.5 for k_t/k_p for the strongly interacting PVP template is close to that found
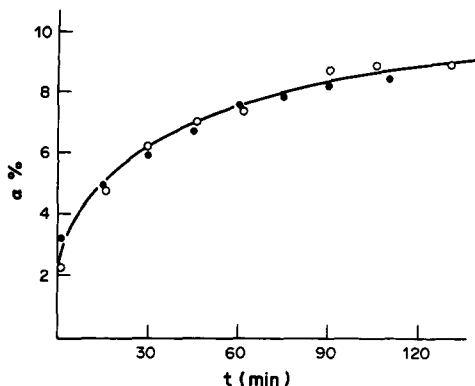
Fig. 6. Conversion in the post-effect for polymerization of MAA with templates: ●, PEG_{20000}; ○, PEGN; without initiators.

Fig. 8. Plot of $(1 - \alpha/v - 1/v_0)$ vs time for polymerization of MAA with PVP as template and UO_2SO_4 as initiator.
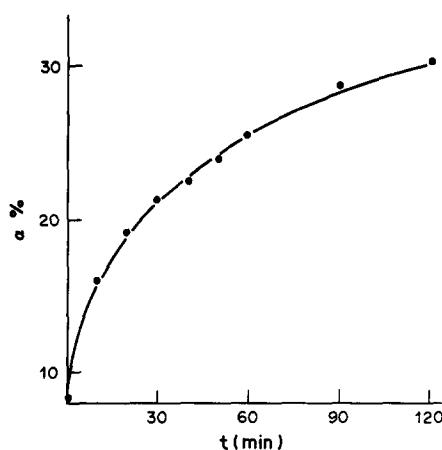
Fig. 7. Conversion in the post-effect for polymerization of MAA with PVP without initiator.

previously (8.3; 8.6) but for the PEG and PEGN templates with a weak monomer–template interaction the values are distinctly different. We have found experimentally that PEG and PEGN templates have no effect on the photopolymerization rate in the presence of photoinitiators despite the fact that they themselves show photoinitiation. This process is so slow that it has no significant effect on the photopolymerization in the presence of photoinitiators. Only PVP affects the photo-polymerization via the monomer–template interaction and as photoinitiator within the range of u.v. radiation wavelengths used.

In further detailed studies including determination of rate constants for elementary processes, these two processes should be taken into consideration.
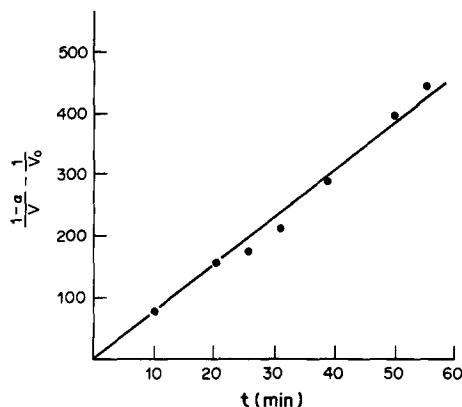
REFERENCES

1. J. Matuszewska-Czerwik and S. Połowiński. *Eur. Polym. J.* **24**, 791 (1988).
2. J. Matuszewska-Czerwik and S. Połowiński. *Eur. Polym. J.* **26**, 549 (1990).
3. Y. Osada, A. D. Antipina, I. M. Papisov, V. A. Kabanov and V. A. Kargin. *Dokl. Akad. Nauk SSSR* **191**, 339 (1970).
4. O. A. Aleksina I. M. Papisov, K. I. Bolyachevskaya and A. B. Zezin. *Vysokomolek. Soedin.* **A15**, 1463 (1973).
5. E. Tsuchida and Y. Osada. *J. Polym. Sci.; Polym. Chem. Edn* **13**, 559 (1975).
6. I. M. Papisov, V. A. Kabanov, Y. Osada, M. Leskanno-Brito, J. Richmond and A. N. Gvozdetskii. *Vysokomolek. Soedin.* **A14**, 1475 (1976).
7. N. Shavit and J. Cohen. *Polymerization of Organized Systems* (edited by H. G. Elias), p. 213. Gordxon and Breach, London (1977).
8. K. Fujimori. *Makromolek. Chem.* **180**, 1743 (1979).
9. J. G. H. M. Lohmeyer, Y. Y. Tan and G. Challa. *J. Macromolec. Sci. Chem.* **A14**, 945 (1980).
10. J. Smid. Thesis, University of Gronningen (1985).
11. J. Gons. Thesis, University of Gronningen (1977).
12. J. Matuszewska-Czerwik and S. Połowiński. *Polimery* (in press).
13. R. B. Whyte and N. W. Mellwille. *J. Sec. Dyers Colour* **65**, 703 (1949).
14. N. P. Galperina, W. F. Grompw, N. M. Homikowski and A. D. Abkin. *Vysokomolek. Soedin* **B17**, 674 (1975).
15. J. Matuszewska-Czerwik and S. Połowiński. *Makromolek. Chem.; Rapid Commun.* **10**, 513 (1989).
16. J. Matuszewska-Czerwik and S. Połowiński. *Polimery* **33**, 397 (1988).