

Polymerization of Asymmetric Tetrafunctional Monomers. I. The Study of Radical Bulk Polymerization of Acrylic and Methacrylic Esters of 2-Allylphenol

O. F. SOLOMON, M. G. CORCIOVEI, and V. TĂRĂRESCU,
Polytechnical Institute "Gh. Gheorghiu-Dej"
Bucharest, Laboratory of Macromolecular Chemistry,
Calea Victoriei 149, București, Romania

Synopsis

The bulk polymerization of 2-allylphenylacrylic ester and of 2-allylphenylmethacrylic ester at 60–80°C. was studied. It was observed that under these conditions azobisisobutyronitrile, lauroyl peroxide, and benzoyl peroxide have satisfactory activity as initiators. The influence of atmospheric oxygen on AOAF and MOAF polymerization was proved. The peculiarities of AOAF and MOAF polymerization (low molecular weight of the soluble polymers which are formed, the absence of gel effect, relatively low critical conversions) may be explained on the basis of chain transfer reactions by the allylic groups.

It is known that the radical bulk polymerization of tetrafunctional monomers occurs with formation of crosslinked, insoluble, and infusible polymers. For this reason this reaction is usually named "crosslinking polymerization" or "three-dimensional polymerization." There are a lot of works dealing with this type of reaction, some of which have a special importance for the explaining of gel-formation, gel-effect, cyclization, and other phenomena which are taking place during the three-dimensional polymerization.¹⁻⁹ The research in this field was directed almost exclusively towards the study of polymerization of symmetric tetrafunctional monomers.

Acrylic and methacrylic esters of 2-allylphenol (AOAF and MOAF) are asymmetric tetrafunctional monomers. The molecules contain two unsaturated, structurally different groups, the allylic and the acrylic (methacrylic) ones, which have a different reactivity in the polymerization reaction.

The synthesis and polymerization of AOAF were not described till now,¹⁰ and very little work has been found on the synthesis and polymerization of MOAF and the properties of respective polymers.^{11,12}

The present work refers to the study of AOAF and MOAF radical bulk polymerization.

Experimental

The MOAF and AOAF synthesis and purification were accomplished according to the method described.^{11,12} In order to reach a higher degree of purity, some additional operations were carried out: an alkaline washing followed by washing with distilled water, drying, and distillation at reduced pressure (10^{-4} mm. Hg) under inert atmosphere without inhibitors.

AOAF: B.p. 88–90°C./0.9 mm.; n_D^{20} 1.5225

MOAF: B.p. 101–102°C./1.5 mm.; n_D^{20} 1.5205

The purity of the monomers has been verified also by gas chromatography.

The following initiators were employed: azobisisobutyronitrile (recrystallized from methanol), benzoyl peroxide (recrystallized from chloroform); lauroyl peroxide, di-*tert*-butyl peroxide, *tert*-butyl-perbenzoate (Elektrochemische Werke München, A.G.), cyclohexanone peroxide (50% in dibutylphthalate), trigonox A-75, and cumene hydroperoxide.

The polymerizations were made in glass tubes. In order to study the reaction in the absence of atmospheric oxygen the tubes were closed after air evacuation at -70°C . and 5×10^{-5} mm. and filled with argon.

After polymerization, the total yield was determined by extraction of the obtained polymer with methanol and the yield in crosslinked polymer was determined by extraction with chloroform.

The molecular weights of soluble polymers were determined cryoscopically in benzene.

Results

The results obtained at the AOAF and MOAF polymerization with different initiators in the presence and in the absence of atmospheric oxygen are shown in Table I. From Table I one can see that for temperatures up

TABLE I
The Activity of Different Initiators in the Bulk AOAF and MOAF Polymerization

Initiator, Cr = 0.5% (to the monomer)	Polymer, %, after 4 hr. at 80°C.			
	Presence of oxygen		Absence of oxygen	
	AOAF	MOAF	AOAF	MOAF
Azobisisobutyronitrile	0	32 ^a	55 ^a	73 ^a
Lauroyl peroxide	8	34.5 ^a	24.5 ^a	43.5 ^a
Benzoyl peroxide	2	18	9	36 ^a
Cyclohexanone peroxide	1.5	3	4	7
Di- <i>tert</i> -butyl peroxide	1	1	1.5	0
<i>tert</i> -Butyl perbenzoate	1.5	1.5	1.5	2
Trigonox A-75 ^b	1	1	3	1
Cumene hydroperoxide	0	1	2	1.5

^a Higher yields than gelation conversions.

^b *tert*-Butyl hydroperoxide, 75% + *tert*-butyl peroxide, 25%.

to 80°C. the following may be considered as initiators with a satisfactory activity: azobisisobutyronitrile (AIBN), lauroyl peroxide (PL), and benzoyl peroxide (PB). One can see also that in the presence of oxygen the AOAF and MOAF polymerization rate is lower than in the absence of the oxygen.

The AOAF behavior by polymerization in the presence of oxygen at higher initiator concentrations may be seen in Table II. According to Table II at 70°C. the polymerization does not take place. At 80°C., and also at higher temperature, the polymerization takes place and the gel formation occurs at lower conversions than in the absence of oxygen.

TABLE II
AOAF Bulk Polymerization in the Presence of Atmospheric Oxygen
with 3% Benzoyl Peroxide

Temperature <i>t</i> , °C.	Time, min.	Polymer, %		Time of gelation, min.
		Total	Cross- linked	
70	1000	0	0	—
80	180	10.5	1	180
90	70	26	12	55
99	30	39	33.5	25

The AOAF behavior in the polymerization reaction with benzoyl peroxide as initiator in the presence of various quantities of oxygen is described in Figure 1. One can see the evident influence of oxygen on the total yield.

As one can observe, increasing of the residual pressure at the air evacuation from the polymerization tubes from 2×10^{-2} to 0.7 mm. Hg has about the same effect on the reaction rate as the diminution of temperature by 10°C.

In the Figure 2 are presented the curves for the conversion MOAF by polymerization with benzoyl peroxide as initiator at 60, 70, and 80°C., the polymerization tubes being conditioned at 5×10^{-5} mm. Hg. In the same figure is also the curve for the MOAF polymerization at 80°C. with the same concentration of benzoyl peroxide in the presence of atmospheric oxygen. The influence of oxygen on the values of the conversion is evident in this case too.

The MOAF bulk polymerization with benzoyl peroxide in the absence of oxygen between 60 and 80°C. verifies the following equation:

$$d[M]/dt = k[I]^{1/2}[M]$$

According to the experimental data we have estimated for this reaction the following values of the total rate constant: $k_{60^\circ} = 0.33$; $k_{70^\circ} = 0.67$; $k_{80^\circ} = 1.36$ l.^{0.5}/mole^{0.5}-min. On the basis of these data one may consider that the reaction is first order towards the monomer concentration and 0.5 order towards the initiator concentration. It was obtained for the overall

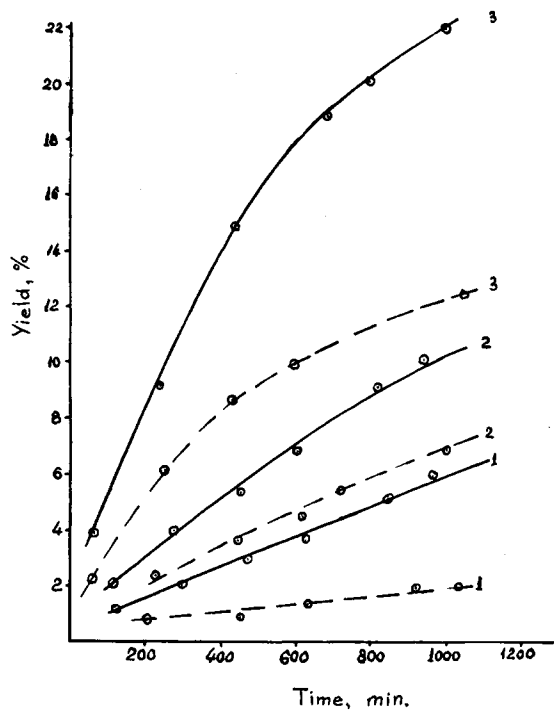


Fig. 1. AOAF polymerization with PB 0.4% (moles): 1, 2, 3: 60, 70, 80°C. (—) The tubes were conditioned at 2.5×10^{-2} mm. (---) The tubes were conditioned at 0.7 mm.

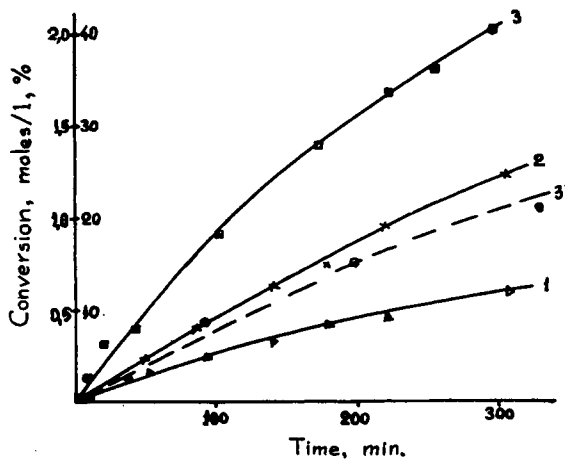


Fig. 2. MOAF polymerization with benzoyl peroxide 0.4% (moles): 1, 2, 3: 60, 70, 80°C., respectively, tubes being conditioned at 5×10^{-5} mm.; 3' -80°C., in the presence of atmospheric oxygen.

energy of activation 16.5 ± 0.5 kcal./mole. The total rate constant of the MOAF polymerization is twice as high on increasing of the temperature by 10°C ., as one can observe from Figure 3.

From the data presented in Figure 4 and Table I, referring to the comparative study of AOAF and MOAF radical bulk polymerization with dif-

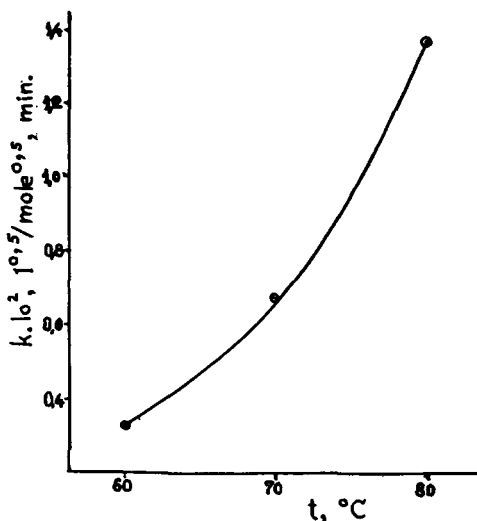


Fig. 3. MOAF polymerization with benzoyl peroxide 0.4% (moles) in the absence of oxygen. The dependence upon temperature of global constant of the reaction rate is shown.

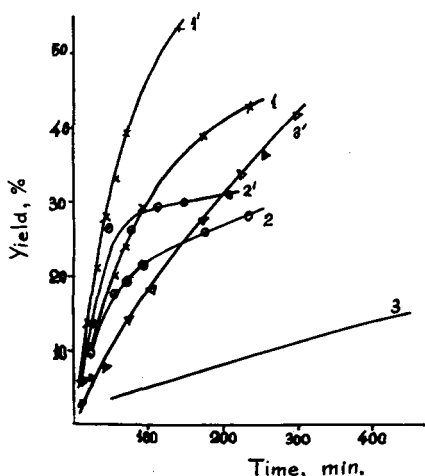


Fig. 4. AOAF and MOAF polymerization with 0.4% (moles) initiator, at 80°C . in the absence of oxygen. 1, 2, 3, AOAF with AIBN, PL, and PB, respectively; 1', 2', 3', MOAF with AIBN, PL, and PB, respectively.

ferent initiators (AIBN, PL, and PB), in the absence of oxygen, one can observe that MOAF is more active than AOAF.

The data presented in Figure 4 show that from the three initiators studied the most active is AIBN, which assures the highest rate of the reaction until at advanced conversions. It follows in the order of their activity lauroyl peroxide and benzoyl peroxide. In the case of PL it is noted that

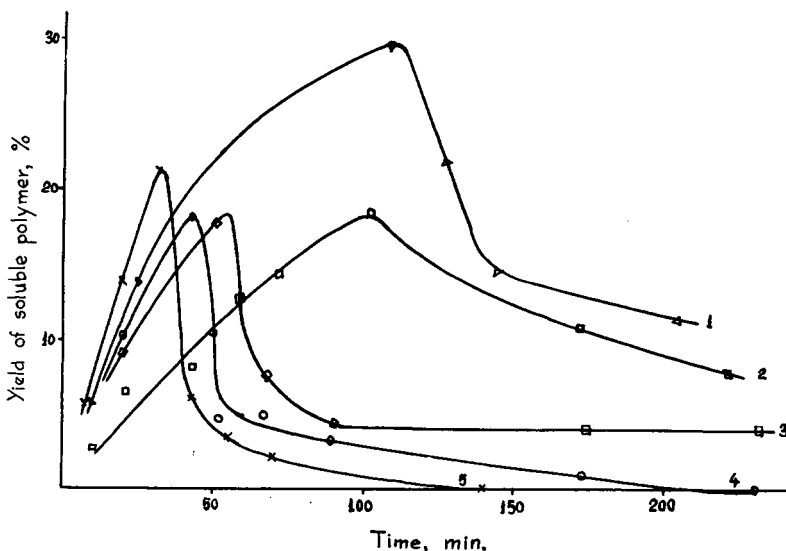


Fig. 5. The variation of the quantities of soluble polymers during the polymerization of AOAF and MOAF with 0.4% (moles) initiator at 80°C. in the absence of oxygen. 1, 2, 5: MOAF with PL, PB, and AIBN, respectively; 3, 4: AOAF with PL and AIBN, respectively.

after reaching of the critical conversion the reaction rate diminishes suddenly. The kinetic activity of AIBN towards PL and PB for conversions up to 20% has the following values:

AOAF polymerization: 1.3 respective 13

MOAF polymerization: 1.3 respective 4

The variation of yield of soluble polymers during the AOAF and MOAF polymerization at 80°C. is represented in Figure 5. As we can see the curves present a first ascendent branch, which is the same as the first part of the curves representing the total yield of the reaction. This first branch ends at the yield corresponding to the critical conversion. Further, the contents of the soluble polymer in the reaction mixture diminishes up to very low values. In the case of initiation by AIBN, the contents of soluble polymer can no longer be detected, a fact which allows one to suppose that in this case the reaction occurs exclusively in the gel phase, probably by the branching of the monomer on the crosslinked polymer already formed.

The critical conversions vary between 18–30%, according to the nature of the monomer and of the initiator. The highest value was observed at the MOAF polymerization with PL as initiator.

The soluble polymers of AOAF and MOAF have melting temperature between 100–130°C. They have the tendency of crosslinking when warmed. Studying them by microscope in polarized light, we observed that they present the birefringency phenomenon. The presence of some crystals in these polymers was verified also by x-ray diffraction. These facts prove the existence of some crystallizable oligomers. In favor of this supposition is the low average molecular weight of soluble AOAF and MOAF polymers: 2500–4000.

The research which was made showed that, after gelation, the reaction occurs especially in the gel phase. The diminution of the reaction rate in the case of PL as initiator may be supposed to be on account of the large molecular volume of this compound and of the respective free radicals, their penetration in the gel phase being difficult.

Discussion and Conclusions

AOAF and MOAF may be polymerized with satisfactory rate at 60–80°C. with azobisisobutyronitrile, lauroyl peroxide, and benzoyl peroxide as initiators. The reaction verifies the classical kinetic laws of radical bulk polymerization.

The atmospheric oxygen has a sensible influence in the development of the reaction, diminishing its rate as one can see from the data presented in Tables I and II and Figures 1 and 2. In the presence of oxygen it was observed that the reaction mixture was yellow or brown-yellow colored.

The considerably lower yields of AOAF and MOAF polymerization in the presence of atmospheric oxygen and also the color which appears under these conditions shows the existence of some possible secondary oxidizing reactions taking place with the simultaneous action of the oxygen, initiator, and temperature over the monomer. We suppose that under these conditions are formed peroxidical compounds whose activity as initiators for the AOAF and MOAF polymerization is different from that of AIBN, PL, or PB. These new peroxides are not active until temperatures of 70°C.

From the data in Table I and Figures 1, 2, and 4 it can be seen that MOAF is more active in the free-radical polymerization than AOAF. This behavior is unusual since it is known that in such reactions the activity of acrylic compounds is higher than that of methacrylic compounds. The reason for this anomaly must be sought in the peculiarities of the studied system, in which the acrylic, respective methacrylic groups are very close to allylic groups. In such a system an intensive chain transfer by the allylic groups is to be supposed. The possibility of inter- and intramolecular ring formation must be considered also.

The radical polymerization of acrylic and methacrylic esters of 2-allylphenol occurs in two steps. In the first step soluble and fusible polymers are formed till the critical conversion is reached when the crosslinked poly-

mer (gel) appears. Furthermore, the polymerization takes place with the formation of crosslinked polymer until the end of the reaction.

From the mechanism point of view, the process may be considered as being composed of three stages:

(a) The polymerization of the most reactive groups (acrylic, respective methacrylic) with rather low participation of allylic groups, especially in the chain transfer reaction. Unsaturated ramified polymers with low molecular weight are probably formed.

(b) Owing to the consumption of acrylic (methacrylic) groups, in the previous stage, their molar ratio in the reaction mixture diminishes by such an amount that the processes continue as a copolymerization of the two structurally different groups. In this step occurs the gel formation and the reaching of high conversion. A relatively slight crosslinked polymer, which contains many unsaturated (especially allylic) groups is formed.

(c) The last step consists of increasing the degree of crosslinking of the polymer by polymerization of its unsaturated groups. Finally an infusible and insoluble polymer with the properties of an organic glass is formed.

It is known that the reactivity of acrylic and methacrylic compounds in the reaction of radical polymerization is much higher than that of allylic compounds. Accordingly, it would have been expected that the asymmetric tetrafunctional acrylic-allylic monomers polymerize with formation of soluble polymers until very high conversions. But the experimental data obtained by us show that, though the critical conversions are higher than those known for symmetric tetrafunctional monomers, their value is, however, low enough. This fact is explained by the very marked chain transfer activity of allylic groups. The transfer by allylic groups may have a double effect: the obtaining of low molecular weight polymers and their reticulation at conversions which are not higher than 30%. Another indirect effect of the chain transfer reaction is the absence of the gel effect: owing to the low molecular weight of the soluble polymers, the viscosity of the reaction mixture cannot reach values which permit the appearance of Trommsdorf's effect. The autoacceleration does not appear even after gelation, because in this stage also the interruption of chain development occurs by the chain transfer reaction. Thus, the lack of mobility of the macroradicals do not have a marked effect on the general rate of reaction.

References

1. W. H. Carothers, *Chem. Rev.*, **8**, 402 (1931).
2. R. G. W. Norrish and E. F. Brookmann, *Proc. Roy. Soc. (London)*, **A163**, 205 (1937); *ibid.*, **A171**, 147 (1939).
3. A. A. Berlin, *Usp. Chimii*, **9**, 642 (1940).
4. P. J. Flory, *J. Am. Chem. Soc.*, **63**, 3083, 3091, 3096 (1941).
5. C. Walling, *J. Am. Chem. Soc.*, **67**, 441 (1945).
6. W. Simpson, T. Holt, and R. J. Zetie, *J. Polymer Sci.*, **10**, 489 (1953).
7. M. Gordon, *J. Chem. Phys.*, **22**, 610 (1954).
8. M. Gordon and R. J. Roe, *J. Polymer Sci.*, **21**, 27, 39, 57, 75 (1956).
9. W. Simpson and T. Holt, *J. Polymer Sci.*, **18**, 335 (1955).

10. O. F. Solomon and M. G. Corciovei, Rumanian patent petition, 1966.
11. V. V. Korshak, S. V. Vinogradova, and M. G. Corciovei, U.S.S.R. Pat. 172311 and 172312 (1965).
12. V. V. Korshak, S. V. Vinogradova, and M. G. Corciovei, *Mat. Plastice (Bucharest)*, 2, 208 (1965).

Résumé

La polymérisation en bloc d'ester de l'acrylate de 2-allylphényl et du méthacrylate de 2-allylphényl à 60–80°C a été étudiée. On a observé que dans ces conditions l'asobisisobutyronitrile, le peroxyde de lauroyle et le peroxyde de benzoyle avaient des propriétés initiatrices satisfaisantes. L'influence de l'oxygène atmosphérique sur la polymérisation AOAF et MOAF a été démontrée. Les particularités de la polymérisation de AOAF et MOAF (faible poids moléculaire des polymères solubles qui sont formés, l'absence d'effet de gel et les conversions critiques relativement basses) peuvent être expliquées sur la base de réactions de transfert de chaîne par les groupes allyliques.

Zusammenfassung

Die Polymerisation von 2-Allylphenylacrylester und 2-Allylphenylmethacrylester in Substanz bei 60–80°C. wurde untersucht. Azobisisobutyronitril, Lauroylperoxyd und Benzoylperoxyd besitzen unter diesen Bedingungen eine befriedigende Aktivität als Initiatoren. Der Einfluss von atmosphärischem Sauerstoff auf die AOAF- und MOAF-Polymerisation wurde nachgewiesen. Die Besonderheiten der AOAF- und MOAF-Polymerisation (niedriges Molekulargewicht der gebildeten löslichen Polymeren, Fehlen eines Geleffektes, verhältnismässig niedrige kritische Umsätze) können auf Grundlage von Kettenübertragungsreaktionen durch die Allylgruppen erklärt werden.

Received December 12, 1966

Prod. No. 1562