Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Photopolymerization of Acrylonitrile: Benzophenone-Isopropanol System as Initiator

C. P. Murthy[a]; B. Sethuram[a]; T. Navaneeth Rao[a]
[a] Department of Chemistry, Osmania University, Hyderabad, India

To cite this Article Murthy, C. P. , Sethuram, B. and Rao, T. Navaneeth(1984) 'Photopolymerization of Acrylonitrile: Benzophenone-Isopropanol System as Initiator', Journal of Macromolecular Science, Part A, 21: 6, 739 — 744

To link to this Article: DOI: 10.1080/00222338408077237

URL: http://dx.doi.org/10.1080/00222338408077237

J. MACROMOL. SCI.–CHEM., A21(6&7), pp. 739-744 (1984)

Photopolymerization of Acrylonitrile: Benzophenone-Isopropanol System as Initiator

C. P. MURTHY, B. SETHURAM, and T. NAVANEETH RAO*

Department of Chemistry
Osmania University
Hyderabad 500007, India

ABSTRACT

Irradiation of benzophenone in the presence of a suitable hydrogen donor like alcohol leads to benzpinacol and the ketone as sole products. This reaction proceeds through ketyl radical intermediates. This photoredox system may be used for photopolymerization. Photopolymerization of acrylonitrile using isopropanol and benzophenone combination as initiator has been studied. The formation of the polymer is directly proportional to irradiation time, [acrylonitrile] and [isopropanol]. The rate of polymerization increases with an increase in concentration of benzophenone to an optimum and a further increase in benzophenone concentration decreases the polymerization rate. A suitable mechanism is suggested.

Irradiation of benzophenone (BP) in the presence of a suitable H-donor leads to benzpinacol and the oxidized alcohol, viz., aldehyde or ketone, as the sole products. This reaction proceeds through ketyl radical intermediates. Such photoredox systems may be considered

---

*To whom correspondence should be addressed.

0022-233X/84/2106-0739$3.50/0

as potential initiators of vinyl polymerization, and the work of Hirano et al. [1] merits special mention. We now report results on the kinetics of photopolymerization of acrylonitrile (AN) using isopropanol (IPA) and benzophenone combination as the initiators.

EXPERIMENTAL

AN and the solvents were purified by standard procedures. BP was purified by recrystallization from ethanol. Photolysis was carried out by using a 500-W medium pressure mercury lamp with an intensity stabilizer (Hannovia make) which had contact with a cooling system. Pyrex tubes (20 mL) were used in a semicircular stand such that the distance of each tube from the source was the same. Standard ferrioxalate actinometry [2] was used to measure the light intensity. The sample solution was 10 mL. Before irradiation, the sample solution was deaerated by bubbling with oxygen-free nitrogen for 15 min. After irradiation the sample solution was filtered through a G 4 sintered crucible, dried at 30°C for 24 h, and weighed. The molecular weight of polymer was determined from the viscosity measurements of a 0.1% solution of poly(AN) in dimethylformamide by using the Mark-Houwink-type [3] relationship between limiting viscosity number and the molecular weight of polymers:

$$[\eta] = 2.43 \times 10^{-4}\ M^{0.66} \text{ at } 25^\circ\text{C}$$

RESULTS AND DISCUSSION

Polymerization did not take place when AN, BP, and IPA were kept in the dark. There was no polymerization even on irradiating the reaction mixture containing BP and AN in dioxane medium. Exposing the monomer to light in the presence of BP and IPA resulted in the formation of poly(AN). The formation of the polymer linearly increased with increasing irradiation time when containing fixed amounts of IPA and AN and at various concentrations of BP (Fig. 1). The slope of these lines gives the polymerization rates. Because these irradiations were carried out in Pyrex tubes, the radiation below 300 nm is cut out, and of the radiation above 300 nm, the 360 nm band is most important. The extinction coefficient of BP at 366 nm is about 100 M^{-1} cm^{-1}. Under the present experimental conditions, the benzpinacol formation proceeds at an insignificant rate. One important observation that can be made from Fig. 1 is that the rate of polymerization increases with an increase in concentration of BP to an optimum and any further increase results in a decrease of the polymerization rate. The polymerization rate increases with an increase in isopropanol concentration (Fig. 2) in 1,4-dioxane when the concentrations of BP

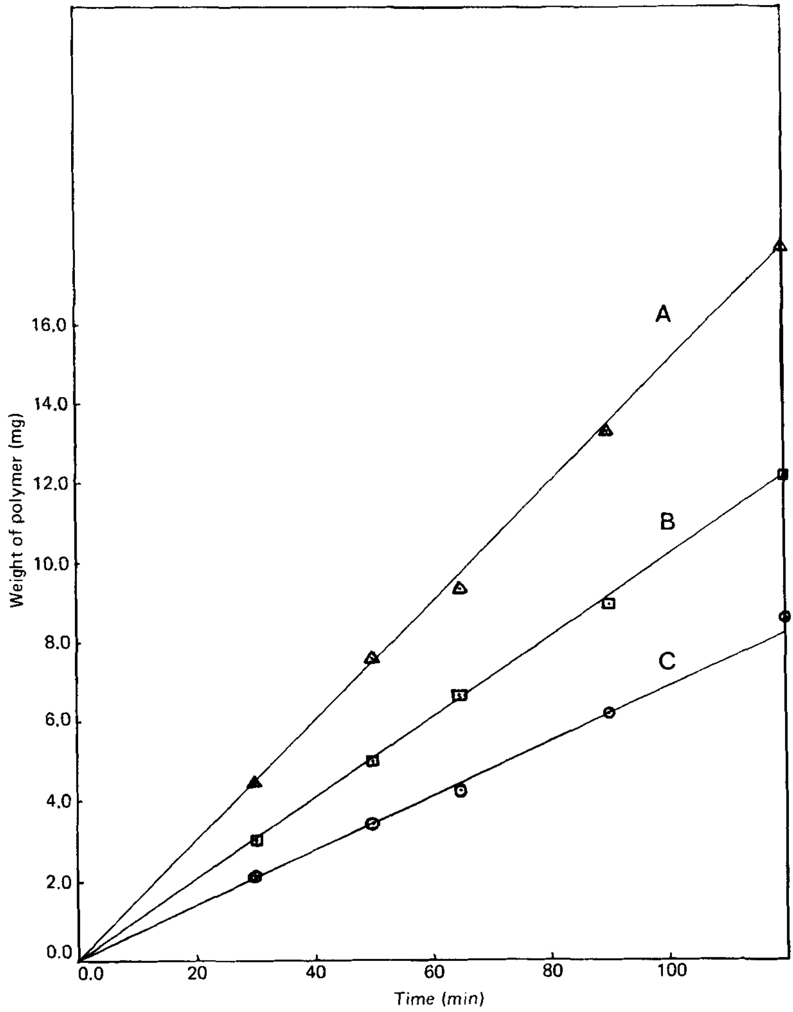

FIG. 1. Effect of irradiation time on polymer yield in 2-propanol solutions with 0.01 M (A), 0.001 M (B), and 0.1 M (C) benzophenone.

and AN is kept constant. When [AN] varied from 0.75 to 3 M while [BP] and [IPA] were kept constant, the rate of polymerization increased linearly with [AN] at low concentrations (Fig. 3). At high concentrations this attained a steady value which may be due to olefin quenching of the excited aromatic ketones.

The absence of polymer formation in the absence of IPA indicates

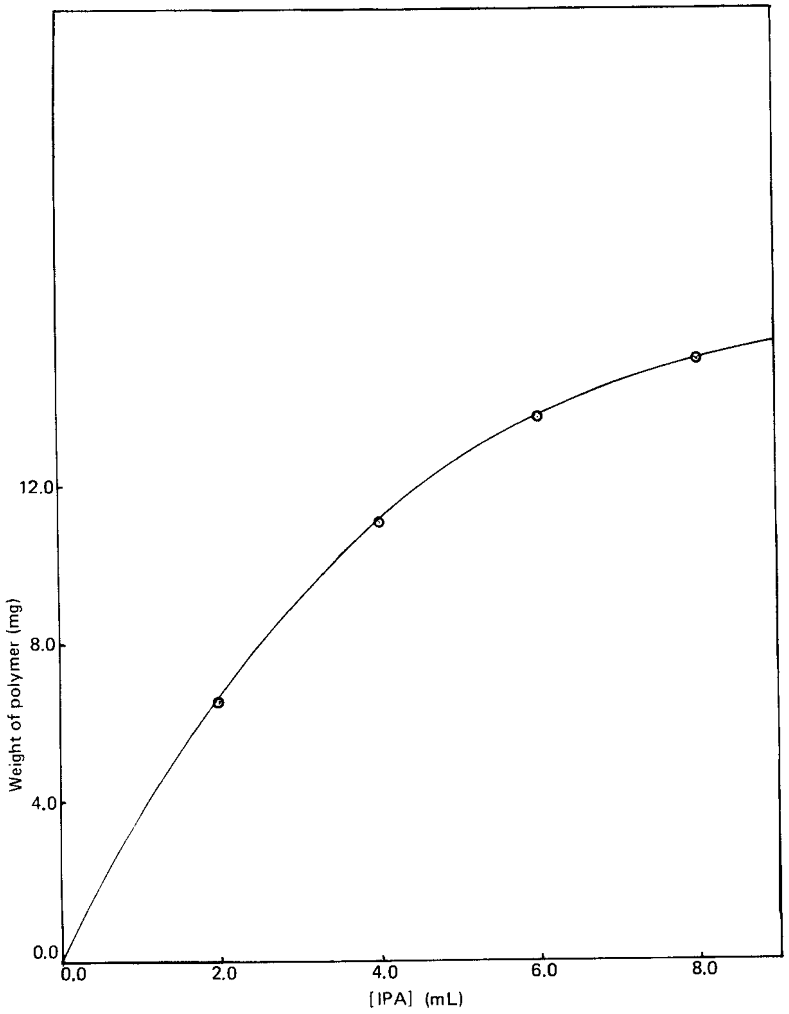

FIG. 2. The dependence of polymerization on 2-propanol in DMSO solution with 0.01 M benzophenone and 3 M acrylonitrile. Reaction time, 100 min; reaction mixture, 10 mL.

that there is no direct photosensitized reaction between BP and AN. The increase in the rate of polymerization with an increase in [IPA] suggests that the initiator comes from the reaction between BP and IPA. It is well known that BP abstracts a proton from IPA, yielding ketyl radicals [4]:

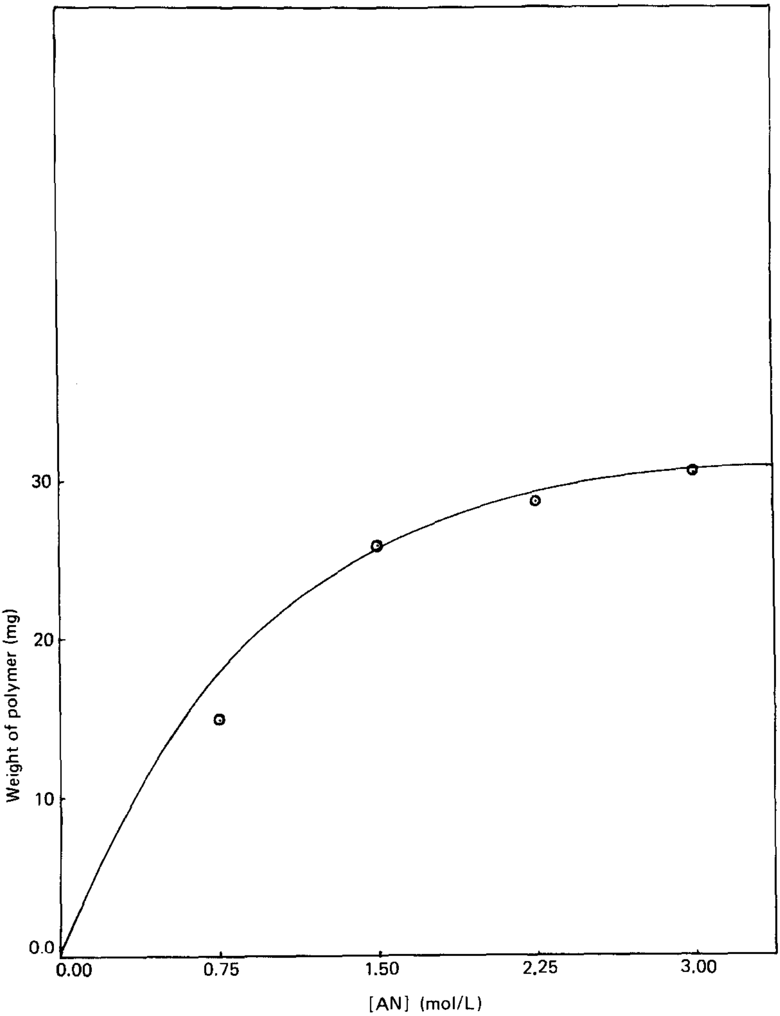

FIG. 3. The dependence of polymer formation on the monomer concentration in 2-propanol solution with 0.01 M benzophenone. Reaction mixture, 20 mL; reaction time, 100 min.

$$\text{BP } (S_0) \xrightarrow{h\nu} \text{BP } (S_1) \tag{1}$$

$$\text{BP } (S_1) \xrightarrow{\text{ISC}} \text{BP } (T_1) \tag{2}$$

$$\mathrm{BP}\ (T_1) + (CH_3)_2CH\text{–}OH \longrightarrow Ar_2\dot{C}\text{–}OH + (CH_3)_2\dot{C}\text{–}OH \quad (3)$$

$$2\,Ar_2\dot{C}\text{–}OH \longrightarrow Ar_2C(OH)\text{–}C(OH)Ar_2 \quad (4)$$

$$2(CH_3)_2\text{–}\dot{C}\text{–}OH \longrightarrow (CH_3)_2\text{–}C{=}O + (CH_3)_2\text{–}C(H)\text{–}OH \quad (5)$$

$$\mathrm{BP}\ (T_1) + Q \longrightarrow \mathrm{BP}\ (S_0) \quad (6)$$

where Q is ground state BP or AN.

Either of the ketyl radicals may initiate polymerization. At constant [IPA] and [AN] the increase in [BP] increased the polymerization to an optimum value and a further increase in [BP] decreased the rate of polymerization (Fig. 1). The increase in the rate of polymerization with an increase in [BP] may be the direct effect of an increase of excited molecules and thereby the number of free radicals. At very high [BP] the self-quenching step (6) also assumes importance. Due to extended conjugation, the diaryl ketyl radical is more stable than the dimethyl ketyl radical. Hence, polymerization may be considered to be the result of aryl ketyl radical initiation.

REFERENCES

[1] K. Hirano, H. Sekino, M. Kurita, Y. Asami, and R. Takagi, Polym. J., 11, 341 (1979).

[2] C. G. Hatchard and C. A. Parker, Proc. R. Soc. (London), A235, 518 (1956).

[3] Houtz, Text. Res. J., 20, 786 (1952).

[4] C. Weismann, E. Bergmann, and Y. Hirshberg, J. Am. Chem. Soc., 60, 1530 (1938).

Accepted by editor October 18, 1983
Received for publication November 18, 1983