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Photocopolymerization of Methyl Vinyl Ketone with Acrylonitrile by Direct Monomer Irradiation

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Summary

Irradiation of methyl vinyl ketone (MVK)/acrylonitrile(AN) mixtures gives facile copolymerization accompanied by small molecule formation. A free radical polymerization mechanism is supported by copolymer formation, absence of solvent polarity effect, and inhibition by TEMPO. Small molecules, presumably cyclobutanes, are favored in dilute solutions and form competitively with copolymer. The excited triplet MVK biradical is identified as the initiating species.

Introduction

Photopolymerizations generally utilize a free radical photoinitiator whose irradiation generates the required initiating free radicals. However, in recent years, direct irradiation of a monomer has come under increasing scrutiny. Such excitation induces singlet to triplet (S → T) intersystem crossing of the monomer to a biradical which is capable of initiating polymerization. Scherzer has established this process for acrylates [1-2]. Chelazzi and his coworkers have shown that even ethylene under high pressure can be polymerized by direct monomer irradiation [3].

In earlier work we established a similar mechanism in the photochemical copolymerization of styrene/ acrylonitrile AN [4], styrene/ fumaronitrile [5], 2-vinylnaphthalene/ AN [6], and 2,3-dimethylbutadiene/AN [7]. In all these systems the UV-active monomer, styrene or 2,3-dimethylbutadiene, was excited by direct irradiation and underwent intersystem to triplet, which then reacts with AN to form a biradical tetramethylene initiating species [8]. Critical in these studies is the fact that the initiating species do not form from irradiation of a charge transfer complex, but irradiation of the monomer itself. We now extend these studies to the copolymerization of another UV–absorbing monomer, methyl vinyl ketone MVK, with acrylonitrile.

Experimental

The experimental procedures have been described previously [4-7]. Methyl vinyl ketone and AN were obtained from Aldrich and purified by distillation. A Conrad-Hanovia 450 W medium pressure mercury vapor lamp served as the light source, 220-280 nm region.

Results

UV Spectroscopy
The UV spectrum of MVK was unchanged by added AN, indicating the absence of a CT complex.

Photo-homopolymerization
Irradiation of bulk MVK for 22 hours at room temperature gave a viscous solution, which upon addition to methanol gave a white fibrous precipitate, indicating high molecular weight. A similar experiment with added benzophenone as a photosensitizer gave a colorless, transparent hard gel. In contrast, irradiation of AN alone gave no polymer.

Free Radical Character of the Photo-copolymerization
Irradiation of a mixture of MVK and AN in bulk gave a viscous, milky, opalescent solution, which gave a fibrous precipitate in methanol. No effect of solvent polarity on the yields of copolymer and cycloadduct was found. Added TEMPO retarded the copolymerization remarkably. This was also observed from the fading of the purplish red color of the TEMPO solution in DCE as irradiation continued.

Table 1. Effect of Solvent on Photo-induced Copolymerizations[a]

Solvent	Yield of Copolymer (%)	Yield Small Molecules (%)
Benzene	24.0	5.7
1,2-DCE	22.0	6.0
Propionitrile	28.0	6.4

[a]Conditions: 1:1 feed of MVK/AN, Total monomer concentration: 4.0 M, irradiation time 10 h

Irradiation of a 3.7 M equimolar solution of MVK/AN in DCE was carried out over a period of 84 hours. The yield of copolymer rose gradually to 67.0% during this irradiation period. The molecular weights were high, as evidenced by the high inherent viscosities, and passed through a shallow maximum at about 30% yield. A small, but significant, amount of small molecules accompanied the copolymer formation. Their yield rose steadily to 6.0%.

Table 2. The Influence of Time on Yields and Inherent Viscosities[a]

Irradiation time (h)	Yield of Copolymer (%)	ηinh (dl/g)	Yield small molecules (%)
4.0	8.1		3.0
8.0	19.6	1.458	3.2
12.0	23.3		4.1
16.0	26.1	1.731	4.2
20.0	32.5		4.6
24.0	34.0		5.1
30.0	39.1	1.566	5.0
48.0	48.1	1.382	5.4
72.0	60.0	1.306	5.7
84.0	67.0	1.273	6.0

[a]Conditions: Solvent: 1,2-dichloroethane DCE, Feed Ratio: 1:1 MVK/AN; Concentration: 3.7 M total

Irradiation of equimolar solutions of methyl vinyl ketone and acrylonitrile was carried out in 1,2-dichloroethane DCE or propionitrile PN at varying total concentrations for 24 hours. Almost identical results were obtained in either PN or DCE as solvents, showing the absence of solvent polarity effect. Copolymer yields rose from ~12% to 37% as total monomer concentration was increased from 2 M to 5.7-6.1 M, while yields of small molecule products accompanying the copolymers declined from > 7 % to ~ 5 %. The copolymers possessed high molecular weight (ηinh 1.60-1.77 dl.g^{-1}).

Table 3. Concentration Dependence of Yields of Copolymer and Small Molecules[a]

Concentration (mol/L)	Solvent	Yield of Copolymer[b] (%)	ηinh (dL/g)	Small molec. (%)
2.0	PN	11.0		7.3
3.0	PN	16.0		6.6
3.94	PN	27.0		6.0
4.80	PN	34.0		5.1
6.1	PN	37.0		5.1
2.1	DCE	13.0	1.60	7.4
2.7	DCE	15.1	1.60	6.4
3.6	DCE	23.7	1.651	6.1
4.2	DCE	31.0	1.663	5.5
4.9	DCE	33.6	1.710	5.0
5.7	DCE	37.1	1.771	4.8

[a] Conditions: Irradiation time: 24 h, Monomer feed ratio: MVK/AN 1:1
[b] Since the composition of copolymers varies, yields of copolymer are calculated based on total starting monomer feed

Finally irradiations were carried out varying the MVK/AN ratio from 0.25 to 4.0 at constant total monomer concentration. The copolymer yield was at a maximum (28.1 %) at a 1:1 ratio. The inherent viscosity also passed through a maximum. Small molecule yields climbed from 2.1 % to 7% as the MVK/AN ratio increased.

Table 4. The Effect of Feed Ratio on the Yield of Copolymer and Small Molecules[a]

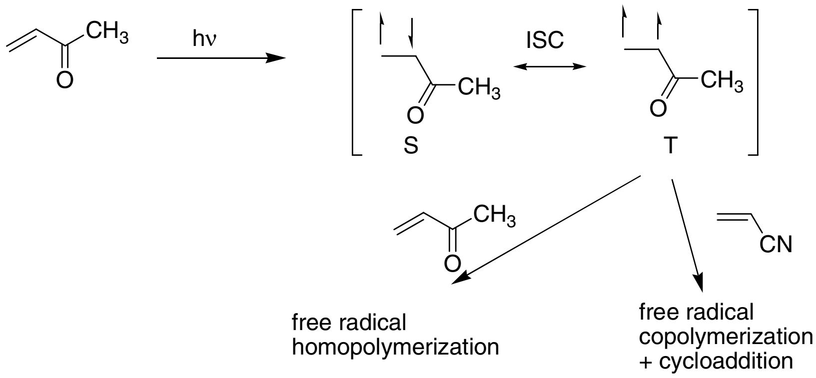
Feed Ratio MVK/AN (mmol/mmol)	Yield of Copolymer[b] (%)	ηinh (dl/g^{-1})	Small molecules (%)	% AN in Copolymer
4.0	11.0	1.30	7.0	
2.0	15.6	1.44	6.3	26.1
1.5	19.0	1.61	6.1	31.2
1.0	28.1	1.70	6.4	43.1
0.5	17.0	1.31	2.9	62.6
0.25	13.0	1.09	2.1	

[a] Conditions: Solvent: DCE, Time 24 h, Total concentration: 3.7 M
[b] Based on the total starting monomer feed

Discussion

Methyl vinyl ketone, like other α,β-unsaturated enones, slips readily into the excited triplet biradical state upon UV irradiation [9-10]. This biradical is twisted, so the two radical centers act as independent monoradicals. Therefore, they represent a particularly favorable case for initiating free radical polymerization or cyclizing to cyclobutanes. This assumption is supported by the fact that MVK alone homopolymerizes when irradiated, i.e. it self-initiates.

Our results show that the yields of both copolymer and small molecules increase with time, and that the yield of polymer increases with overall concentration. The yield of small molecules passes through a maximum and declines. This is because at higher concentration the monomer can trap the biradical before it cyclizes, and initiate co-polymerization.



The reactivity ratios at 60 °C are known for the copolymerization of MVK (m_1) and AN (m_2), $r_1 = 1.78$ and $r_2 = 0.61$ [11]. These reactivity ratios show that MVK prefers to homopropagate, while AN radical can add to either monomer. The maximum yield of 28% at equimolar MVK/AN reflects a balance between increased initiation rate as MVK concentration rises, because of self-initiation and preferred homopropagation, and a faster cross-propagation rate with AN.

Because the small molecules formed in very low yield, they were not investigated in detail. They are presumed to be cyclobutanes formed by $\pi^2 + \pi^2$ cycloadditions, as is well known for α,β-unsaturated ketones, and could be both MVK homodimers and MVK/AN cross dimers [12-13].

The overall results are completely consistent with and extend our earlier studies. In each case, upon irradiation the monomer forms a triplet biradical, which partitions between initiation and cyclization.

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