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Radical Addition to 2-Isopropenyl-5-Butoxyoxazole

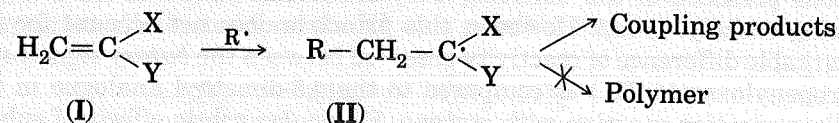
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Synopsis

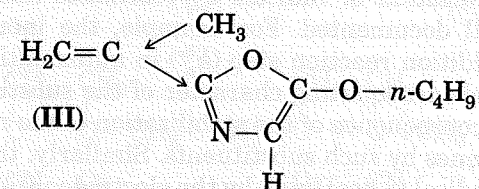
The preparation and the spectroscopic analysis of a dimeric adduct (V) obtained from 2-isopropenyl-5-butoxyoxazole (III) and α, α' -azobis-isobutyronitrile (AIBN) (IV) are reported. It is noteworthy that (III) inhibits completely the homopolymerization of styrene. This is in strong opposition to the facile homopolymerization and copolymerization of 2-isopropenyl-4,6-dimethyloxazole with styrene. The smooth formation of (V) is also in sharp contrast to the lack of reactivity of (III) towards cationic initiators.

INTRODUCTION

The term merostabilization has been suggested to describe the stabilization imparted to free radicals and radical-like species bearing substituents of opposite electron requirement.¹ In particular, this concept has been used to explain the preferential dimerization of the primary radicals resulting from the interaction between a radical precursor and an olefin such as (I) (with X = donor and Y = acceptor).^{1b}



The easy availability of such an olefin (III) in our laboratories² prompted us to study its reactivity towards polymerization initiators.

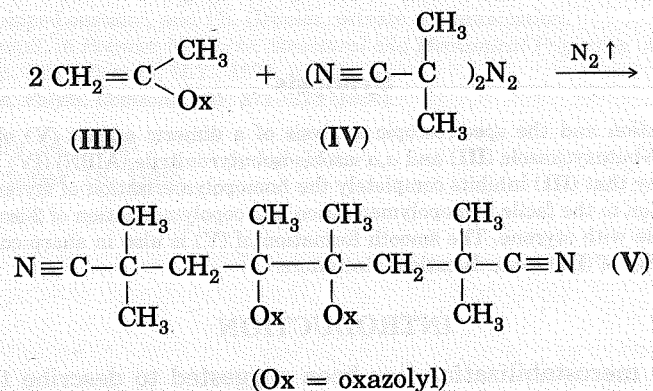


RESULTS AND DISCUSSION

The isopropenylbutoxyoxazole (III) did not polymerize thermally or photochemically in the presence of a catalytic amount of α,α' -azobis-isobutyronitrile (AIBN) (IV) or of benzoyl-peroxide as radicals precursors.

Moreover, **III** completely inhibits the thermal homopolymerization of styrene by AIBN [**III**]: styrene = 1:1]. These results are in strong contrast with the facile homopolymerization and copolymerization reactions of 2-isopropenyl-4,5-dimethyloxazole by the same initiator at 70°C.³

On the other hand, **III** reacts smoothly at 76°C with AIBN to afford the dimer of the addition product of an isobutyronitrile radical:



The very effective stabilizing effect of captodative substituents has been stressed in many cases.^{1b} It would be therefore tempting to invoke this principle in the present case to explain the lack of reactivity of **III** for radical polymerization as the radical **II** should be stabilized by the simultaneous presence of the donating CH₃ substituent and of the electroattracting oxazolyl group. However, this principle does not account for the remarkable difference of reactivity observed between the *butoxy* substituted isopropenyloxazole (**III**) as compared to the 4,5-dimethyl analogue in the copolymerization reaction with styrene. Particular subtle effects of substituents are therefore acting at the kinetic level. For example, a substantial complementary stabilization of the radical **II** by the *butoxy* substituent can be considered.

In fact, the stabilization of radicals by resonance and electrodonating substituents is well documented. For example, the increase of the rate constant for the addition reaction step (k_p^{br}) in autoxidation of substituted styrenes with the electrodonating character of the substituents⁶ has been interpreted as the consequence of the stabilization of the radical addition product to the styrenes by such substituents. Similarly, the stabilization of the intermediate radical (3 kcal/mol) by the electrodonating methoxy group explains the higher reactivity of *p*-methoxytoluene as compared to *p*-methyltoluene (1.5 kcal/mol relatively to toluene) in hydrogen abstraction by the *t*-butoxy radical⁷ as well as the much higher reactivity of *p*-methoxyphenyl relatively to the *p*-methyl substituted analogue for H-abstraction by the styrylperoxy radical.⁸

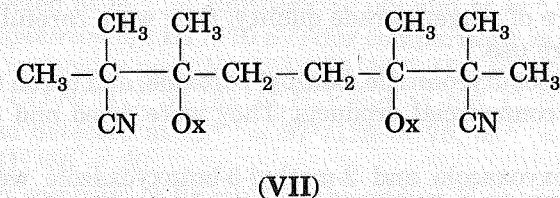
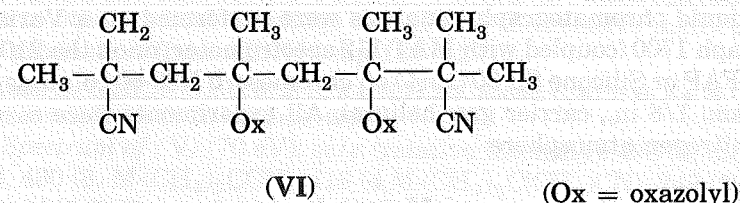
Therefore, the lack of reactivity of **III** (as compared to 2-propenyl-4,5-dimethyloxazole) for radical copolymerization with styrene can be interpreted as the result of a strong stabilization of the intermediate radical by the *butoxy* group, the addition reaction to styrene being consequently impeded relatively to the dimerization reaction. Owing however to the ob-

served large difference of reactivity of both reagents, particular effects such as the participation of the *butoxy* group to the preferential solvation of the radical **II** could also cooperate to the enhancement of the dimerization reaction relatively to the addition process, interactions between the more polar *butoxy* substituted oxazolyl moieties being favored. Similarly, lipophilic type interactions should also be considered: the nonpolar dimethyl substituents of the oxazole ring would favor the interaction of the oxazole monomer with the (nonpolar) styrene system promoting therefore the copolymerization pathway in this case. The importance of lipophilic type interaction particularly in biochemistry (active sites of enzymes) and in organic chemistry⁹ is now well established.

The possibility of a direct participation of the heterocycle group of **III** as inhibitor has been eliminated as 2-methyl-5-butoxyoxazole has no effect on the polymerization of styrene initiated by AIBN. It is also noteworthy that **III** does not polymerize either in the presence of a cationic catalyst such as boron trifluoride etherate as expected from the basic properties of the oxazole ring.

The structure of the adduct **V** was established by elemental analysis, molecular weight determinations and spectroscopic data (see Experimental part).

Both ¹H-NMR and ¹³C-NMR spectra show the occurrence of an oxazole ring of a *butoxy* radical and of a nitrile group (also detected by IR spectroscopy), as well as the disappearance of the vinyl function. Moreover, ¹H-NMR analysis reveals the presence of a unique AB system due to the presence of an asymmetrical center close to a methylene group. This last observation eliminates formula **VI** as a possible structure.



Mass spectrometry gives a fragmentation pattern which is compatible with structure **V** and allows the rejecting of formula **VI** and **VII**. The study of the fragmentation mode shows indeed that the ion ($m/e = 249$) resulting from the symmetrical cleavage of molecule **V** is relatively abundant whereas formulas **VI** and **VII** should give preferentially fragments at $m/e = 68$ and 430. Moreover, the presence of two metastable peaks at $m^+ = 193^2/249 = 149$ and at $m^+ = 165^2/193 = 142$ in the spectrum confirms that

the two main signals result from the successive loss of a 1-butene molecule and of a carbon monoxide molecule from this initially formed radical.

Confirmation of structure **V** for the adduct was obtained by an x-ray analysis which has been published elsewhere.⁴ In fact, such a structure was also expected on the basis of the well-known more important stabilization of tertiary radicals relatively to secondary ones.

CONCLUSION

The ready formation of the adduct **V** from the oxazole **III** and AIBN is the result of a tail-to-tail dimerization of an initial radical addition product. However, the unexpected inhibition of the homopolymerization of styrene by **III** shows that importance of remote electronic (and/or polar interaction) factors is particularly determining in the present case which cannot be interpreted solely on the basis of the captodative theory.

EXPERIMENTAL

Microanalyses were performed by the Centre Interservice d'Analyses Organiques (University of Liège). High resolution mass spectra were obtained from Dr. J. Pecher (University of Brussels).

IR, UV, and low resolution mass spectra were recorded on a Perkin-Elmer model 21, Varian Techtron 635 and Varian MAT-112 spectrometers respectively. ¹H-NMR and ¹³C-NMR spectra were taken using Varian HA-100 and Brücker HFX90 instruments. Melting points (uncorrected) were determined using a Leitz Wetzlar microscope. Some molecular weight determinations were also made in toluene at 45°C on a DAMPFDRUCK OSMOMETER KNAUER instrument.

Gas liquid chromatography analysis were performed on a Varian chromatograph 1700 (coupled with MAT-112 spectrometer) or on the 2100 model using FFAP or Silicone SE 30 (15%) on chromosorb N30-60 columns (length: 4 ft, diam: 1/8 in., carrier gas: helium). All experiments were carried out under nitrogen atmosphere.

Materials

All the solvents were of reagent-grade quality: they were carefully dried and degased just before use.

Styrene, α,α' -azobis-isobutyronitrile, benzoyl peroxide, and boron trifluoride etherate were all commercial products. They were dried and purified by classical methods.

2-Isopropenyl-5-butoxyoxazole and 2-methyl-5-butoxyoxazole were synthesized as reported.² They were purified by repeated distillations *in vacuo* in the presence of calcium hydride.

Attempts of Radical Polymerization of (III)

The attempts of radical polymerization of **III** were performed thermally (at 76°C) or photochemically (at 25°C) in the presence of benzoyl peroxide or of α,α' -azobis-isobutyronitrile (2 mol % based on total monomer) in a benzene solution of **III** (0.54M). No polymer could be precipitated by pouring the solution into heptane or methanol after 50 h of reaction.

Attempts of Radical Copolymerization of (III)

The attempts of radical copolymerization of **III** with styrene were carried out at 70°C in the presence of AIBN (2 mol % based on total monomer) in a benzene solution of **III** (0.27M) containing styrene (0.27M). No polymer could be obtained by pouring the solution into heptane or methanol after 50 h.

Radical Polymerization of Styrene in the Presence of 2-Methyl-5-Butoxyoxazole

Radical polymerization of styrene was performed at 70°C in the presence of AIBN (1 mol % based on total monomer) in a benzene solution of 2-methyl-5-butoxyoxazole (0.27M) containing styrene (0.27M) (98%). Pure polystyrene was obtained by precipitation with methanol after 50 h.

Attempts of Cationic Polymerization of (III)

The attempts of cationic polymerization of **III** were carried out at 71°C in the presence of borontrifluoride etherate (2 mol % based on total monomer) in a benzene solution of **III** (0.35M). No polymer could be precipitated by pouring the solution into heptane or methanol after 40 h.

Preparation of (V)

AIBN (**IV**) (1.85 mmol) is added to 2-isopropenyl-5-butoxyoxazole (**III**) (4.1 mmol) in benzene (10 mL) at 76°C: a quantitative amount of nitrogen (95%) is recovered within 15 min. **V** is isolated by evaporation of benzene and recrystallization in benzene-heptane. Yield: 30% (the balance probably corresponds to other radical couplings and also to the relative inefficiency in radicals production from AIBN⁵). mp 126–127°C.

ANAL. Calcd. for $C_{28}H_{42}N_4O_4$: C, 67.5; H, 8.4; N, 11.2%. Found: C, 67.7; H, 8.4; N, 11.0%. M (tonometry in toluene at 45°C): 460 (calcd: 498).

Mass Spectrum of (**V**) (70 eV): m/e (relative intensity): 498 (4, molecular peak M), 430 (8, M-(CH₃)₂CCN), 416 (4, M-(CH₃)₂C(CH₂)CN), 249 (20, M/2), 193 (100, M/2-C₄H₈), and 165 (16, M/2-C₄H₈-CO). Metastable peaks were also detected at $m^+ = 193^2/249 = 149$ and at $m^+ = 165^2/193 = 142$.

Mass spectrum of (**III**) (70 eV) (for comparison): m/e (relative intensity): 181 (29, molecular peak M), 125 (100, M-C₄H₈), 97 (27, M-C₄H₈-CO), 69 (65, M-C₄H₈-CO-NCH₂), 56 (23, C₄H₈) and 41 (96, C₃H₅-). Metastable peaks were also detected at $m^+ = 97^2/125 = 75$, $m^+ = 69^2/97 = 49$ and at $m^+ = 41^2/56 = 30$.

The IR spectrum (KBr mull) of the adduct **V** shows the disappearance of the out of plane bending band (898 cm⁻¹) of the vinyl group of **III** but the other bands of **III** are still observed. The typical absorption of the nitrile group occurs at 2250 cm⁻¹.

The UV spectra were recorded with solutions of **III** and of the adduct **V** in ethanol **III**: $\lambda_{max} = 276$ (log₁₀ $\epsilon = 3.93$) and 195 (log₁₀ $\epsilon = 3.79$) nm; (**V**): $\lambda_{max} = 234$ (log₁₀ $\epsilon = 4.17$) and 195 [log₁₀ $\epsilon = 3.92$] nm].

¹H-NMR spectrum of (**V**) (100 MHz) shows signals in CDCl₃ at δ (int. TMS) = 0.96 (t, 3H, CH₂-CH₃), 1.03 (s, 3H, CH₃), 1.29 (d, 1H, B of AB, $J_{AB} = 14.3$ Hz, (CH₃)₂C(CN)-CH₂), 1.40 (s, 3H, CH₃), 1.60 (m, 4H, O-CH₂-CH₂-

CH_2-CH_3), 1.62(s,3H, CH_3), 2.52 (d,1H,A of AB, $J_{AB} = 14.3$ Hz, $(\text{CH}_3)_2\text{C}(\text{CN})-\text{CH}_2$), 4.01(t,2H, $\text{O}-\text{CH}_2-\text{CH}_2$) and 6.04 (s,1H,CH heterocycle) ppm.

$^1\text{H-NMR}$ spectrum of (III) (100 MHz) (for comparison) shows peaks in CDCl_3 at δ (int.TMS) = 0.96 (high order t), 3H, CH_2-CH_3), 1.6 (m,4H, $\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 2.08 (d of d, $^4J_{AX} = 1.5$ Hz and $^4J_{MX} = 1.4$ Hz, 3H, $(\text{CH}_3)\text{C}=\text{CH}_2$), 4.04 (t,2H, OCH_2), 5.21 and 5.71 (2m, $^2J_{AM} = 0.5$ Hz, 2H, $(\text{CH}_3)\text{C}-\text{CH}_2$) and 6.09(s,1H,CH heterocycle) ppm.

$^{13}\text{C-NMR}$ spectrum of (V) shows signals in CDCl_3 at δ (int.TMS) = 13.6, 17.7, 18.8, 25.9, 30.1, 34.1 (two peaks), 43.3 and 47.6 (9 saturated carbons), 72.3 ($\text{O}-\text{CH}_2$), 99.5 (CH heterocycle), 1.25 (C—N) and 155 and 159 (C—2 and C—5 heterocycles) ppm.

$^{13}\text{C-NMR}$ spectrum of (III) (for comparison) shows signals in CDCl_3 at δ (int.TMS) = 13.7, 18.6, 19.0 ($\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$), 31.1 ($\text{CH}_2 = \text{CH}_2 = \text{C}(\text{CH}_3)$), 72.0 ($\text{O}-\text{CH}_2$), 100.3 (CH heterocycle), 115.5 ($\text{CH}_2 = \text{C}(\text{CH}_3)$), 131.7 ($\text{CH}_2 = \text{C}(\text{CH}_3)$) and 153.8 and 160.0 (C-2 and C-5 heterocycle) ppm.

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Monomer Chain Transfer in the Copolymerization of Styrene and Butyl Acrylate

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Synopsis

Free radical chain transfer constants have been measured by copolymerizing styrene and butyl acrylate in emulsion at 60°C. Some improvements to this experimental technique are reported and estimates are given of the sensitivity of the calculated values to experimental uncertainties. Monomer chain transfer constants were found to be 1.2×10^{-4} (styrene) and 2.5×10^{-4} (butyl acrylate). The sum of the cross-transfer constants is 2.7×10^{-4} . The activation energy for chain transfer to styrene monomer is found to be 24 Kcal/mol in the 44°–60°C range.

INTRODUCTION

The industrial importance of styrene-acrylic copolymers makes for interest in the kinetics of free radical polymerizations of such monomers. Chain transfer to monomer sets an upper limit to the molecular weight that can be attained in the polymerization or copolymerization of these monomers. These chain-transfer constants are measured often from intercepts of plots of number average degree of polymerization against rate of polymerization. Application of such data to copolymerizations suffers from the neglect of cross-transfer reactions. Here we report monomer transfer constants for reaction of polystyryl and poly(butyl acrylyl) radicals with their corresponding monomers as well as cross-transfer rates with the unlike monomers. This is an application of an emulsion copolymerization technique that has been employed previously in the styrene/methyl methacrylate and styrene/alpha-methylstyrene systems.^{1,2} The technique is further refined here. A sensitivity analysis is reported for this method and the activation energy for chain transfer to styrene monomer is measured.

Theory

Earlier articles from this laboratory^{1,2} should be consulted for derivations of the basic equations used in this study. Straightforward application of the simple copolymer model^{3,4} permits estimation of transfer constants between each monomer and macroradical in the system. The method hinges on the difference between the rate of initiation of macroradicals (or termination, under steady-state conditions) and the quotient of the rate of copolymerization divided by the number-average degree of polymerization of the copolymer that is produced:

$$R_{tr} = \frac{R_p}{\bar{X}_n} - \frac{R_i}{n} \quad (1)$$