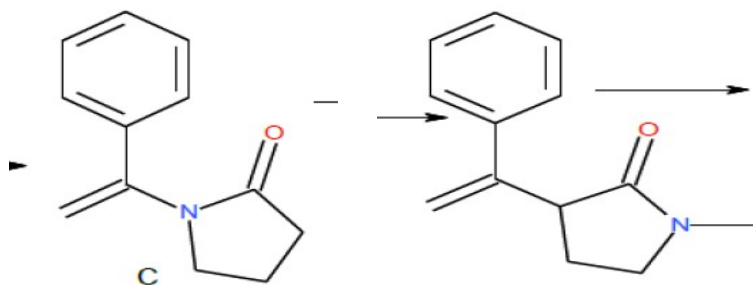


Captodative 1,1-Vinyl Monomers

By: Robert B. Login rloginconsulting.com

In a previous pdf (New Pyrrolidone Vinyl Monomers, rloginconsulting.com), I described a series of captodative monomers based on lactams especially pyrrolidone. I found a reference that claimed they would readily polymerize by a free radical mechanism. I think other structures that I'm going to suggest, would also polymerize and would be worth consideration.



The above are from that pdf and are captodative (electron donating and withdrawing substituents on the same carbon) examples. You could replace the benzene with other electron donating compounds and likewise the electron withdrawing pyrrolidone with other effective compounds.

What follows is my searched for examples in the literature (that was available to me).

“In the copolymerization of styrene and α -substituted methyl acrylates the reactivities of the esters towards the styryl radical are influenced by both the steric and the polar nature of the α -substituent, and, with the exception of α -phenyl methyl acrylate, follow a modified Taft equation of the form $\log \dots$ ”

Cameron, G. G., & Kerr, G. P. (1967). The copolymerization behavior of α -substituted methyl acrylates. *European Polymer Journal*, 3(1), 1-4.

Abstract

“The relative reactivities of α -substituted methyl acrylates toward styrene radical decrease in the following order of the substituents $C_6H_5 \gg CH_3 > C_6H_5CH_2 > H \sim C_2H_5 \sim n-C_3H_7 \sim n-C_4H_9 > i-C_4H_9 > cyclo-C_6H_{11} > i-C_3H_7 > sec-C_4H_9$. The order can mostly be explained in terms of a steric effect. A linear relationship between the relative reactivities and TAFT's steric parameters has been found with the exception of a few α -substituents.”

Chikanishi, K., & Tsuruta, T. (1965). Reactivity of α -alkylacrylic esters. II. Copolymerization behaviors of methyl α -alkylacrylates. *Die Makromolekulare Chemie: Macromolecular Chemistry and Physics*, 81(1), 211-222.

Reactivity of Methyl α -Alkylacrylates in Polymerization

By KUNIO CHIKANISHI and TEIJI TSURUTA

(Eingegangen am 28. Dezember 1963)

There has been little work only on the polymerization of α -alkylacrylic esters other than α -methylacrylate. CRAWFORD¹⁾ and HOLMES-WALKER²⁾ reported that methyl α -*tert*-butylacrylate formed only its dimer or trimer, if at all, in the presence of radical initiators or of sodium dissolved in liquid ammonia. α -Ethyl- and α -phenyl-acrylic esters³⁾ are also unknown to undergo homopolymerization to solid high polymers under radical polymerization conditions. This communication is concerned with polymerization behaviour of various α -alkylacrylic esters.

Table 1. Homopolymerization of Methyl α -Alkylacrylates,
 $\text{CH}_2=\text{C}(\text{R})\text{CO}_2\text{CH}_3$

R	Polymerizability ^{a)}	
	Radical ^{b)}	Anionic ^{c)}
H	⊙	⊙
CH ₃	⊙	⊙
C ₂ H ₅	○	⊙
n-C ₃ H ₇	○	⊙
iso-C ₃ H ₇	×	×
n-C ₄ H ₉	⊗	○
iso-C ₄ H ₉	×	○
sec-C ₄ H ₉	×	×
C ₆ H ₅	○	⊙
C ₆ H ₅ CH ₂	○	○
cyclo-C ₆ H ₁₁	×	×

^{a)} ⊙: Polymerizes to high polymer.

○: Polymerizes slowly to low polymer.

⊗: Some indications for oligomer formation.

×: No polymerization.

^{b)} AIBN, 0.6 mole-%; at 65 °C. for 15 days.

^{c)} e.g., *n*-butyl Li, 3–5 mole-%; at –78 °C. for about 1 week.

The above are some of the earliest references I found(both were not available in their entirety; however).

Conclusions

“The results presented in this paper demonstrate how delicate the factors determining the free-radical polymerizability of a substituted acrylic monomer can be. The steric bulk of the substituent placed at the α -position clearly plays a major role, but predictions are difficult when a new substituent able to display both inductive, mesomeric, and steric effects is introduced for the first time. In this study, we demonstrated that a large substituent like a trimethylsiloxy group can be introduced without preventing the

polymerizability as long as primary linear esters are concerned. When large substituents were placed on the ester, a dramatic decrease in polymerizability was observed.

A study of the polymerization kinetics has revealed some unusual features (nonfirst-order kinetics, solvent dependence of the rate of polymerization) that were rationalized on the basis of the steric hindrance introduced by the substituents and of the high captodative stabilization of the propagating radicals.”

Penelle, J., Verraver, S., Raucq, P., & Marchand-Brynaert, J. (1995). Free-radical polymerization of acrylates α -substituted by trimethylsiloxy substituents. Dramatic influence of the size of the ester substituent on the polymerizability. *Macromolecular Chemistry and Physics*, 196(3), 857-867.

“MEA together with those of methyl α -(2-carbomethoxyethyl) acrylate (MMEA), methyl α -[2,2-bis(carbomethoxy)ethyl]acrylate [M(DM)EA], and methyl α -[2,2,2-tris(carboethoxy)ethyl]acrylate [M(TE)EA]. MEA polymerizes slowly to low molecular weight as previously reported by Penelle *et al.* However, MMEA and M(DM)EA yielded higher molecular weight polymers at the much faster rates than MEA. These monomers bearing large α -substituents yield the polymers through the *steric hindrance-assisted polymerization.*”

Kobatake, S., & Yamada, B. (1996). Sterically hindered elementary reactions in radical polymerization of α -ethylacrylic esters as studied by ESR spectroscopy. *Polymer journal*, 28(6), 535-542.

I take this to mean that large ester groups can improve captodative polymerizability. However this reference also reviews other captodative monomers:

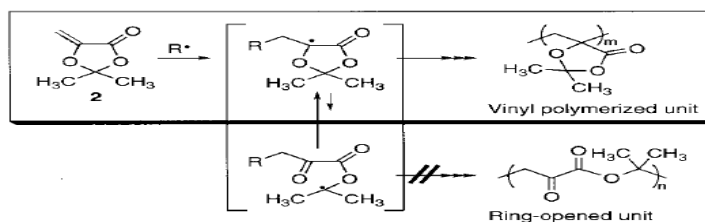
(substituted methyl)acrylates bearing alkoxymethyl, ²

acyloxymethyl,³ fluoromethyl,⁴ and carboalkoxymethyl groups,⁵ as the IX-substituent readily polymerize to high molecular weight in spite of the presence of the bulky substituent.

They are not however talking about the acrylate ester group which in this case is methyl.

Kobatake, S., & Yamada, B. (1996). Radical polymerization and copolymerization of methyl α -(2-carbomethoxyethyl) acrylate, a dimer of methyl acrylate, as a polymerizable α -substituted acrylate. *Journal of Polymer Science Part A: Polymer Chemistry*, 34(1), 95-108. This is another example.

The above reference suggests that this monomer with a alpha ethyl(methylcarboxy) instead of just an ethyl 1,1 methyl acrylate is more reactive as a free-radical monomer because of electronic effects even though its a bigger group than the ethyl?



Scheme 3

This monomer is also captodative.

Miyagawa, T., Sanda, F., & Endo, T. (2000). Synthesis and radical polymerization of 5-methylene-2, 2-dimethyl-1, 3-

dioxolan-4-one. *Journal of Polymer Science Part A: Polymer Chemistry*, 38(10), 1861-1865.

Smith, Q., Huang, J., Matyjaszewski, K., & Loo, Y. L. (2005). Controlled radical polymerization and copolymerization of 5-methylene-2-phenyl-1, 3-dioxolan-4-one by ATRP. *Macromolecules*, 38(13), 5581-5586.

Britner, J., & Ritter, H. (2016). Methylene lactide: vinyl polymerization and spatial reactivity effects. *Beilstein journal of organic chemistry*, 12(1), 2378-2389.

“Abstract

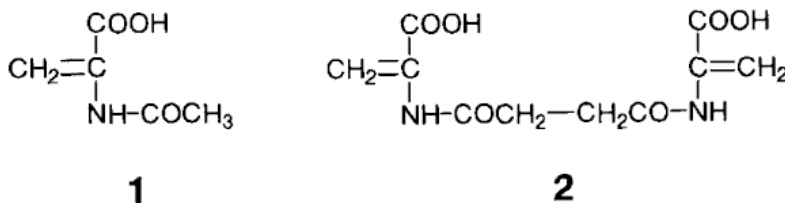
A series of α -alkylacrylates, including methyl ethacrylate (MEA), methyl α -propylacrylate, methyl α -isopropylacrylate (MiPA), methyl α -butylacrylate (MnBA), and methyl α -isobutylacrylate (MiBA), were successfully polymerized at 65 °C under high pressure (1–9 kbar). In contrast to results obtained at ambient pressure, all monomers yielded high molecular weight polymers (number-average molecular weight = 4–18 $\times 10^4$), except for MiPA (number-average molecular weight = 8 $\times 10^3$), probably because of the high steric hindrance of the isopropyl group.”

Rzayev, J., & Penelle, J. (2002). Polymerization of sterically congested α -alkylacrylates under high pressure. *Journal of Polymer Science Part A: Polymer Chemistry*, 40(7), 836-843.

(I don't have the entire reference just this abstract)

Rzayev, J. (2004). *Controlled free-radical polymerization at high pressures: Synthesis and properties of poly (α -substituted acrylates)*. University of Massachusetts Amherst.

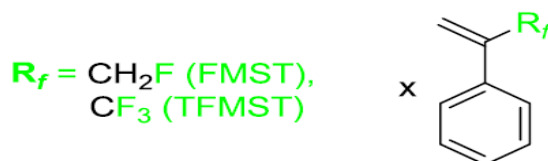
been prepared. In particular, dehydroalanine polymers have potentially hydrophilic groups, and may be expected to form the hydrogel which shows a high swelling ratio and good mechanical properties due to a long polymer chain with low concentration of cross-linking. This



Schem 1.

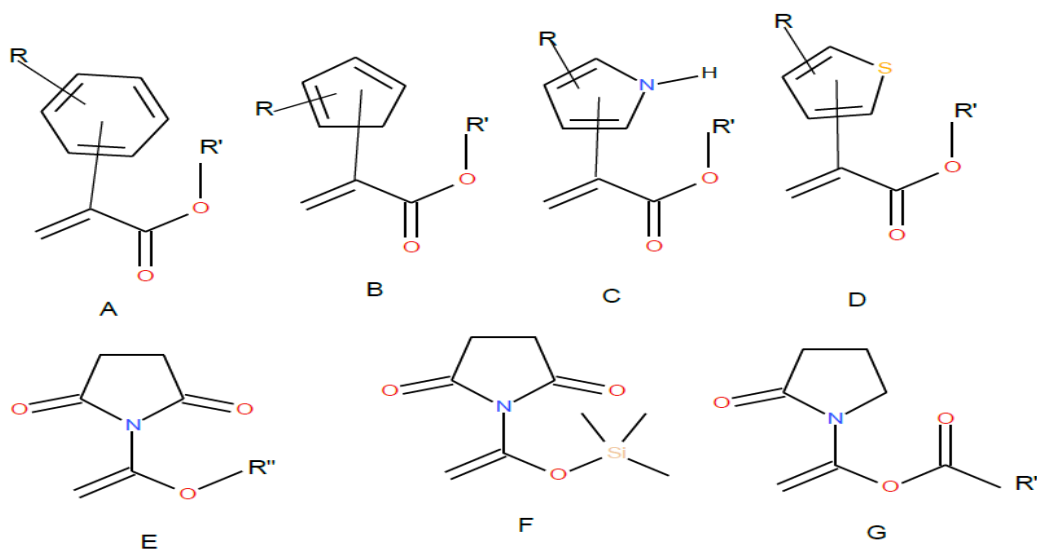
“This shows that dehydroalanine is also a CD monomer.

Tanaka, H., Suzuka, T., Hada, K., & Tezuka, Y. (2000). Kinetic study on free radical polymerization of 2-acetamidoacrylic acid and formation of hydrogel. *Polymer journal*, 32(5), 391-394.



Walkowiak-Kulikowska, J., Szwajca, A., Gouverneur, V., & Ameduri, B. (2017). Synthesis, characterization, and thermal and surface properties of co- and terpolymers based on fluorinated α -methylstyrenes and styrene. *Polymer Chemistry*, 8(42), 6558-6569.

Wolska, J., Walkowiak-Kulikowska, J., Szwajca, A., Koroniak, H., & Améduri, B. (2018). Aromatic fluorocopolymers based on α -(difluoromethyl) styrene and styrene: synthesis, characterization, and thermal and surface properties.



Scheme 1: Several ideas for CD Monomers.

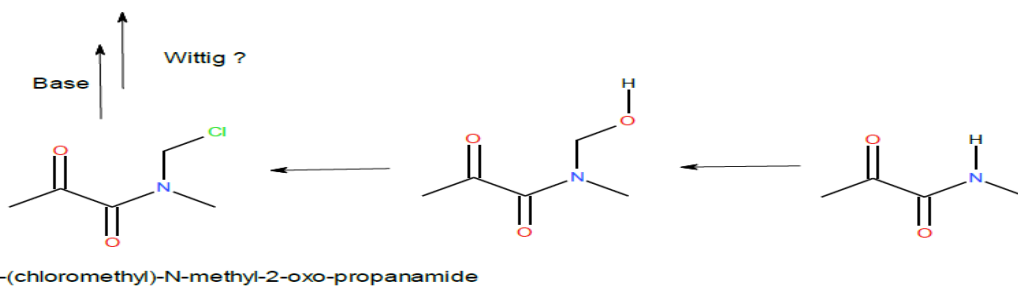
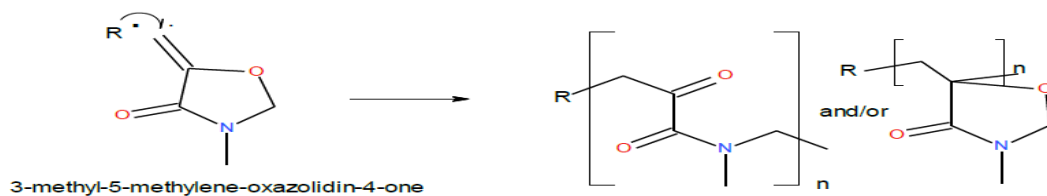
The above could very well polymerize as FR monomers and/or by high pressure. The main problem I have is what could you use the resulting polymers or copolymers of the above for? A is a known monomer and some derivatives were found and C&D are in SciFinder with little information and just the name of a supposed supplier. I searched the internet, Scifinder, wherever I had access with very little if any results.

E,F&G are vinyl ethers but still could polymerize by a FR mechanism. After polymerization F could lose the Si protecting group to afford hydroxyls on the polymer backbone. It is known to do this in one of the above references. You could replace monomers like E,F&G with the aromatic heterocycles. This would afford water soluble OH groups on the polymer backbone.

I would also think that R' could be hydrogen resulting a carboxylic acid that would afford water solubility upon neutralization.

Monomers A-D could afford polymers compatible with those compounds containing heterocycles used in conductive polymers, solar cells etc. They could be complexed to some extent with water soluble or dispersible polymers of A-D or related types.

And finally, I've searched for the following monomer but have not found any references. So I think this is a new idea for CD FR monomer.



Scheme 2: There must be other ways to synthesize this monomer but I would bet that its easily FR polymerized!

Thank you for reading these proposals. Comments and corrections or advice is welcomed!

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