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PR Number: 97PR06480-00

Technical Report #86

ANIONIC PHOTOPOLYMERIZATION OF METHYL-2-CYANOACRYLATE
AND SIMULTANEOUS COLOR FORMATION

by

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Macromolecules 2000, 33, 7761-7764

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Date Submitted:

November, 2000

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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
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1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 11/15/00		3. REPORT TYPE AND DATES COVERED Technical Report
4. TITLE AND SUBTITLE ANIONIC PHOTOPOLYMERIZATION OF METHYL-2-CYANOACRYLATE AND SIMULTANEOUS COLOR FORMATION			5. FUNDING NUMBERS G# N00014-97-1-0834 PR #: 97PR06480-00	
6. AUTHOR(S) Viktor V. Jarikov and Douglas C. Neckers				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESSES(S) Center for Photochemical Sciences Bowling Green State University Bowling Green, OH 43403			8. PERFORMING ORGANIZATION REPORT NUMBER 86	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESSES(S) Department of the Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Anionic polymerization of methyl-2-cyanoacrylate initiated by photoinduced heterolysis of crystal violet leuconitrile (CVCN) and of malachite green leucohydroxide (MGOH) is demonstrated. Polymerization is accompanied by color formation.				
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13. ABSTRACT (Maximum of 200 words)				
14. SUBJECT TERMS			15. NUMBER OF PAGES: 4 16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

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Macromolecules[®]

Reprinted from
Volume 33, Number 21, Pages 7761-7764

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Received July 11, 2000

ABSTRACT: Anionic polymerization of methyl 2-cyanoacrylate initiated by photoinduced heterolysis of crystal violet leuconitrile (CVCN) and of malachite green leucohydroxide (MGOH) is demonstrated. Polymerization is accompanied by color formation.

Introduction

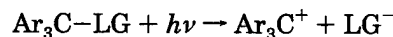
The past two decades have seen dramatic advances in the application of photochemical processes in the preparation of materials for coatings, surface modification and combinatorial processes, integrated circuits, data storage, digital optical recording, stereolithography, holography, and chemical sensors based on fiber optics.^{2–4} Many systems used in such processes involve radiation curing. The most common monomers are acrylates, and these are polymerized by radical chain reactions.⁵ Though photoinduced cationic polymerizations⁶ now contribute ~10% market share, reports of photoinduced anionic polymerizations are rare.^{7–10} Photoinitiated anionic polymerizations have been briefly reviewed.^{11–14}

For some years we have been interested in concomitant polymerization and selective coloration.^{4,15} The notion is to selectively color individual volumes of photopolymers concomitantly with their formation. As in the case of a 2D color photograph, the idea is to produce an authentic color replica but to do so in three dimensions. Our initial objective was to selectively color volumes in stereolithography models so that they could be specifically identified.

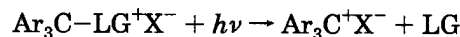
Simultaneous free radical polymerization of acrylates and color formation from leucolactones of triaryl-methane (TAM) dyes has already been successfully demonstrated with oxidizing agents such as iodonium salts^{15–17} and is commercial. In such reactions, the photon-absorbing lactone becomes an electron donor in the excited state, and the initial reaction is electron transfer to the iodonium salt. Subsequent reactions convert the reduced iodonium salt to radicals and the lactone radical cation to the colored cation. A similar process, which forms color and radicals, can be accomplished via oxidation of TAM leuco dyes by halogenated hydrocarbons.^{18–20} Leucolactones have also been reported to be opened photochemically by irradiating an acid generator such as anthracene-bound sulfonium salt and 2,6-dinitrobenzyl tosylate²¹ in their presence.¹⁵ Resins that can be colored and cured in a single photoinduced step may find numerous applications. The formation of a colored shaped plastic is especially desirable in those applications where color visualization is critical.^{22–24}

It is well-known that TAM dyes can be prepared by direct irradiation of colorless leuconitriles, leucocarinols, and leucoethers since this leads to heterolysis (ionization).^{20,25,34} This is a ubiquitous phenomenon in that

structurally similar xanthene and acridine leuco dyes undergo a similar process. We surmised, therefore, that the photoinduced heterolytic cleavage of the dye-leaving group (dye-LG) bond in colorless nitriles, carbinols, thiols, ethers, esters, azides, ammonium salts, phosphonium salts, and the like could be employed in the simultaneous generation of color and a reactive nucleophilic species:



or



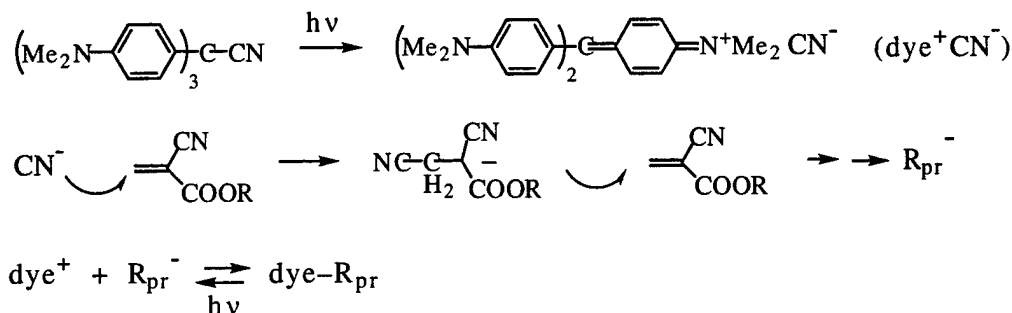
where Ar_3C^+ = R_2N -substituted TAM, xanthene, or acridine dye and LG^- = CN^- , $-\text{CH}_2\text{COR}$, HO^- , HS^- , RO^- , RS^- , RCOO^- ; LG = pyr, NR_3 , SR_2 , PR_3 and X^- = BF_4^- , AsF_6^- , ClO_4^- .

Nucleophiles such as CN^- , RO^- , NR_3 , and PR_3 are known to polymerize cyanoacrylates, cyanoacetylene, acrolein, acrylonitriles, formaldehyde, *N*-phenylmaleimide, propiolaldehyde, isocyanates, epoxides, methacrylates, nitrostyrene, *N*-alkenamide, methacrylamide, crotonaldehyde, dialkylmethylenemalonate, *N*-acylethylene imine, cyanoformamidyl, etc.²⁶ Thiulates and malonates act as initiators for the polymerization of *n*-butyl acrylate.²⁷ Since most of the nucleophiles that can be generated by the heterolysis of TAM leuco dyes are known to initiate anionic polymerization with appropriate monomers, we thought this is a route to photoinitiated anionic polymer formation.²⁰

As we have indicated, literature reports of anionic photopolymerization are rare. It was reported that photogeneration of thiocyanate⁸ from $\text{K}^+[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$, pyridine¹⁰ from $\text{W}(\text{CO})_5\text{py}$, PPh_3 and 2-methylpyridine from heterolytic decomposition of phosphonium and *N*-ethoxy-2-methylpyridinium salts, respectively,⁷ and acac^- from $\text{Pt}(\text{acac})_2$ ⁹ led to a rapid polymerization of neat cyanoacrylate monomer. Photogeneration of bases such as amines has been utilized for base-catalyzed polymerizations and cross-linking.²⁸ There are no commercial applications of anionic photopolymerization of which we are aware. Scheme 1 exemplifies how the anionic polymerization of cyanoacrylate might be induced via photoheterolysis of a leuco dye such as CVCN.

Results and Discussion

Photogeneration of CN^- and OH^- in Methyl 2-Cyanoacrylate (M-2-CA). Photolysis was conducted

Scheme 1. Anionic Polymerization of Cyanoacrylate via the Photoionization of CVCN (NB: in the Absence of H⁺ Donors Such as Water, Alcohol, etc.)

in NMR tubes in a Rayonet photoreactor ($\lambda_{\text{exc}} = 280\text{--}320$ nm, Pyrex glass filter) and was followed by NMR with TMS as an internal standard. Irradiation of a solution of M-2-CA, CVCN, and SO₂ in CDCl₃ (0.09, 4.5 $\times 10^{-3}$, and 4 $\times 10^{-5}$ M, respectively; 5 h) led to total conversion of CVCN into CV⁺. Since the monomer concentration decreased only by one-quarter and all of CVCN was converted to CV⁺CN[−] (5 mol % with respect to the monomer), this implied that 25% of the M-2-CA was converted, on average, into pentamers. On the other hand, photolysis of M-2-CA and CVCN (0.1 and 5 $\times 10^{-3}$ M) in CDCl₃ in the presence of CD₃OD (0.28 M) led to the conversion of half of the monomer, indicating formation, on average, of decamers. In this case, the initiating species could be either CN[−] or CD₃O[−]. It is well-known that leuco dyes such as CVCN undergo photooxidation in the presence of halogenated solvents,^{18,20} so CDCl₃ was a poor choice of solvent since one generates CV⁺Cl[−] in lieu of CV⁺CN[−]. With Cl[−] being substantially less nucleophilic/basic than CN[−], polymerization is sure to be less efficient.

Similar experiments with malachite green leucohydroxide instead of CVCN produced rapid thermal polymerization (~5 min) upon addition of MGOH (5 $\times 10^{-3}$ M) to the 0.1 M solution of M-2-CA in CDCl₃. However, a similar solution in benzene-*d*₆ was thermally stable. Subsequent 2 h photolysis led to complete disappearance of both monomer and the leucohydroxide and extensive dark-green precipitate. Presumably, MG⁺-dyed cyanoacrylate polymer was formed. The yield of the polymer was 97 wt %, and it had a MW of 2 $\times 10^3$ (PDI ~ 3.5) as determined by GPC. The main peak had a broad shoulder centered at ~6 $\times 10^3$. Complete conversion of the monomer may be attributed to the greater nucleophilicity of OH[−]. In control reactions carried out under identical conditions in the absence of CVCN or MGOH, there was no significant decrease of M-2-CA concentration. The intensely colored dark-green precipitate was filtered, and the color did not exhibit any visual fading for a few weeks while stored in room atmosphere in the absence of light. The fading of color was notably accelerated when the precipitate was exposed to room light, which is consistent with poor light fastness of malachite green dye. The color of the polymer disappeared even faster upon dissolution in acetone or acetonitrile. This is expected on the basis of the known thermal and photoinduced reactions of MG⁺ with nucleophiles and oxygen.

Homolysis of the dye–LG bond competes with heterolysis, and both are singlet excited-state reactions.^{20,25} The relative amount of each reaction is solvent-dependent because heterolysis is strongly affected by the polarity of the environment. Thus, M-2-CA might have

been polymerized by both radical²⁹ and anionic mechanisms in less polar solvents. However, our previous work suggested that homolysis is either inefficient or followed by a rapid in-cage recombination of the singlet radical pair.^{20,30} Hence, the radical mechanism is likely to be of decreased importance.

Effect of CV⁺ on Polymerization of M-2-CA. Na⁺ and Li⁺ are generally the counteranions in anionic thermal polymerizations. Since both the free anion and the ion pair are thought to contribute to chain propagation, one anticipates that the counteranion plays an important role.³¹ This is confirmed by the work of Warmkessel, who showed that the relative rate of termination of anionic polymerization (the ratio of rate constants of termination and propagation) decreases from Li⁺ to Cs⁺.³² In another recent investigation, metal-free anionic polymerization of MMA initiated in the presence of the bulky counteranion tetraphenylphosphonium produced excellent results.³¹ In our case TAM, xanthene, or acridine dye cation would be expected to be noninterfering. Because these cations are electrophilic but large and bulky, the additional termination route provided via reaction with propagating anions would be likely of decreased importance. The adduct of counteranion to polymer chain is expected to be photoreactive in its own right and could contribute to the photoionization reaction as well (Scheme 1). Therefore, the nucleophiles generated in our system would effectively initiate polymerization, and the dye cations would ineffectively quench the propagating anions. The last postulate was tested as follows.

Several poly(cyanoacrylate) polymers were synthesized in the presence or absence of CV⁺BPh₄[−] in order to compare their MW's and MWD's. The starting monomer mixture consisted of M-2-CA, THF (solvent), *p*-TsOH (inhibitor), and SO₂ (stabilizer) (Table 1). Tributylamine was used as initiator. The same synthetic scheme was repeated without inhibitor, without stabilizer, and with the monomer being added to THF or THF added to the monomer. In control experiments the glassware and stirrers were washed with acid (acidified), or not washed with acid, to test the results. Analysis (GPC) showed that the presence of CV⁺BPh₄[−] had a negligible effect on MW and MWD of the poly(cyanoacrylate) polymers in all the cases. Both with and without dye present, the polymer was formed repeatedly and reproducibly in three fractions with MW = 3.5 $\times 10^6$ (~20%), 1.5 $\times 10^4$ (~10%), and 4.5 $\times 10^3$ (~70%). Polydispersities of all the fractions varied from 2 to 4. In the absence of the initiator the starting monomer mixture started to solidify in about a week when kept on the benchtop in a closed vial.

Table 1. Synthesis of Cyanoacrylate Polymers 1–4 in THF^a

component	1	2	3	4
M-2-CA	0.066 M	0.067 M	0.22 M	0.22 M
SO ₂ (stabilizer)	2.9×10^{-5} M, 0.044%	3.0×10^{-5} M, 0.044%	9.6×10^{-5} M, 0.044%	9.6×10^{-5} M, 0.044%
<i>p</i> -TsOH (inhibitor)	6.29×10^{-5} M, 0.095%	6.5×10^{-5} M, 0.096%	9.81×10^{-6} M, 0.0045%	9.79×10^{-6} M, 0.0045%
NBu ₃ (initiator)	6.27×10^{-4} M, 0.95%	6.5×10^{-4} M, 0.96%	1.02×10^{-3} M, 0.47%	1.01×10^{-3} M, 0.47%
CV ⁺ BPh ₄ [−] (additive)	0	6.65×10^{-4} M, 0.99%	0	1.05×10^{-3} M, 0.49%

^a Absolute concentrations; percent molar with respect to the monomer.

Control Experiments: Stability of M-2-CA. NMR experiments revealed that nonirradiated M-2-CA is not stable at room temperature in dry CDCl₃:CD₃CN = 3:1 (by weight) or in dry CDCl₃:CD₃COCN = 4:1. Under these conditions the monomer disappeared in several minutes. In neat acetonitrile, cyanoacrylate was completely consumed in 5–7 min. The monomer, however, is stable for a week in chloroform and in CDCl₃:CD₃CN = 5:1 and much longer in C₆D₆. It appears that polarity of the environment determines thermal stability of the monomer. However, traces of water might have played a role also, although we kept the conditions as anhydrous as possible. Also, one should keep in mind that CDCl₃ contributes DCl impurity, which further inhibits spontaneous thermal polymerization. Another possible conclusion for systems containing acetonitrile has to do with weak basicity of this solvent: acetonitrile may not be basic enough to initiate polymerization in less polar solvents but is basic enough to initiate polymerization in more polar ones.

We also found that nonirradiated *N,N*-dimethyl-*p*-toluidine, Michler's ketone (*p*-Me₂NPh)₂CO, and CVCN do not initiate polymerization of the monomer dissolved in CDCl₃. The presence of CVCN does not lead to polymerization of M-2-CA in THF-*d*₈ either. On the other hand, tributylamine and triethylamine initiate the thermal polymerization process instantaneously even in nonpolar solvents.

CVCN and M-2-CA. Upon addition of crystalline powder of CVCN to neat M-2-CA (stabilized with 4×10^{-3} M SO₂), polymer formed instantaneously on the surface of the CVCN. The dimethylanilino groups of CVCN are likely basic enough to initiate polymerization in the polar monomer environment. Since this could be prevented by the addition of an inhibiting acid, colorless polymer was only produced when a solution of *p*-TsOH or HCl:CVCN = 2:1 (molar) in the neat monomer (CVCN:monomer = 1:100 by weight) was irradiated for 20 min. The same colorless polymer resulted from irradiation of a similar mixture in 1:1 cyanoacrylate and THF, but in this case there was an initially formed violet color of moderate intensity that disappeared during further irradiation.

In attempt to prevent the spontaneous thermal polymerization of M-2-CA, we prepared a TAM dye leuconitrile containing less nucleophilic amino groups. Conversion to amides, carbamates, sulfonamides, 2,5-dimethylpyrrole, or attaching bulky protective groups (can be photolabile) reduces basicity and nucleophilicity of an amino group.³³ The trityl group was chosen as one of the most promising sterically hindered protective groups. Reaction of rhodamine 6G leuconitrile with trityl bromide in anhydrous THF in the presence of NEt₃ at 60 °C failed to yield the ditritylated adduct. However, basic fuchsin leuconitrile and leuco trityl ether, both protected with three trityl groups (*p*-TrNHPPh)₃CCN and (*p*-TrNHPPh)₃COTr, were successfully prepared. These were shown to generate an intense red-blue color as

efficiently as basic fuchsin leuconitrile itself both in solution and even in polymerizing viscous epoxy resin. Unfortunately, the spontaneous thermal polymerization of neat M-2-CA persisted, and additional investigation is required to clarify the reasons. Possibly, water was present in the trace amounts and was deprotonated by the trityl-protected amino groups. This released the initiating species, OH[−]. Therefore, we expect electron-withdrawing protective groups to enhance thermal stability better than sterically demanding protective groups.

Conclusions

We have demonstrated that anions produced by the photolysis of crystal violet leuconitrile (CVCN) and malachite green leucohydroxide (MGOH) show significant potential for the controlled anionic polymerization of cyanoacrylates such as methyl 2-cyanoacrylate. Having the colored polymer obtained from irradiation of a solution of MGOH in benzene in the presence of M-2-CA, we have demonstrated the principle of simultaneous photoinduced anionic polymerization and color formation. Thermal anionic polymerization of M-2-CA initiated by trialkylamines is indifferent to the presence of CV⁺ in the polymerizing monomer. Polymerizations with neat monomer have presented difficulties in that it was hard to control the dark reaction and coloration. Currently work to resolve these issues is underway.

Experimental Section

Monomer was purchased from Polysciences, Inc., and used without further purification. CVCN [tris(4-*N,N*-dimethylanilino)phenyl]acetonitrile and BFCN [tris(4-aminophenyl)acetonitrile] were prepared previously.³⁰ Pure MGOH [bis(4-*N,N*-dimethylaminophenyl)phenylmethyl alcohol] was prepared according to the known procedure.³⁴ Both the compounds and deuterated solvents were kept in a chamber with P₂O₅, and their NMR spectra were taken prior to experiments to ensure total absence of water peaks. Benzene and THF were distilled from sodium/benzophenone. NMR spectra were taken with a Varian Gemini 200 NMR spectrometer. GC/MS and DIP/MS were taken on an HP 5988 mass spectrometer coupled to an HP 5880A GC and interfaced to an HP 2623A data processor. UV-vis spectra were obtained using an HP 8452 diode array spectrophotometer. Infrared spectrometry was performed using a Mattson Instruments 6020 Galaxy series FT-IR spectrometer. Melting points were determined using a capillary melting point apparatus (Uni-melt, Arthur H. Thomas Co., Philadelphia, PA) and were uncorrected. HPLC and GPC were performed with an HP 1050 series instrument equipped with multiple wavelength diode-array and refractive index detectors. For GPC, the instrument was equipped with 300 × 7.5 mm PLgel 5 μ-mixed C column. Acetone or acetonitrile was used as the mobile phase, and the flow rate was 0.8 mL/min. Polystyrene samples of known MW were used for MW calibration.

Photolyses of air-saturated solutions were performed in a Rayonet RPR-100 photoreactor (a merry-go-round apparatus) equipped with 14 filter-coated GE (21 W), low-pressure

mercury UV bulbs ($\lambda_{\text{exc}} = 280\text{--}320\text{ nm}$). Vials, quartz test tubes (10 mL), Pyrex NMR tubes, and microscope glass plates all dried were used as photolysis vessels (tubes sealed with a rubber septum). Compounds were characterized by ^1H and ^{13}C NMR, mass, IR, and UV-vis spectroscopy, elemental analysis, and TLC. The disappearance of the starting materials and appearance of products was monitored by HPLC and NMR.

Tris(4-*N*-tritylamino-phenyl)acetonitrile. BFCN was dissolved in anhydrous THF, and triethylamine was added followed by the solution of trityl bromide in THF, BFCN:TrBr:NEt₃ = 1:3:10. THF was partially evaporated, and triethylammonium bromide was filtered. Hexanes were added to the mother liquor, and the precipitate was cold-recrystallized from dichloromethane-methanol and then from dichloromethane-hexanes.³³ (*p*-TrNHPPh)₃CCN (95% yield): ^1H NMR (200 MHz, CDCl₃) δ 7.36–7.10 (m, 45H), 6.43 (d, $J = 8.8\text{ Hz}$, 6H), 6.17 (d, $J = 8.8\text{ Hz}$, 6H), 4.95 (s, 3H); ^{13}C NMR (APT, 50 MHz, CDCl₃) δ 145.6, 145.2, 129.8, 129.1, 128.4, 127.8, 126.7, 124.4 (CN), 115.8, 71.6, 54.7; IR (KBr) cm^{-1} 3398, 3055, 3022, 2233 (CN), 1608, 1509, 1489, 1446, 1321, 1302, 1255, 1184, 1030, 900, 818, 761, 750, 700, 636; MS (EI, MW is 1040, instrumental maximum is 900) 797 (–Tr), 554 (–2Tr), 479, 466, 390, 314, 298, 243 (b), 228, 215, 165 (b), 119; mp = 176–178 °C. Anal. Calcd for C₇₇H₆₀N₄: C, 88.81; H, 5.80; N, 5.38. Found: C, 88.51; H, 5.67; N, 5.45.

Poly(cyanoacrylate). Vial and stirrer were soaked in hydrochloric acid and dried. THF solution of *p*-TsOH was placed in the vial and diluted. Solution of CV⁺BPh₄[–] was added where needed followed by fresh M-2-CA. The vial was sonicated for 10 min. Solution of amine was quickly delivered with intensive stirring. After 30 min, THF was evaporated, and the residue was dissolved in the minimal amount of acetonitrile. Either chloroform or diethyl ether was added, and the white solid was filtered and dried in vacuo.

Acknowledgment. We thank Drs. George S. Hammond and Thomas H. Kinstle for insightful discussions. This research was supported by the McMaster Endowment, the National Science Foundation (DMR-9526755), and the Office of Naval Research (Navy N00014-97-1-0834).

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MA0012090