

Methyl Ketone-Photosensitized Polymerization of N-Methylolacrylamide with Cotton*

ROBERT M. REINHARDT, JETT C. ARTHUR, JR., and OSCAR HINOJOSA, *Southern Regional Research Center, Science and Education Administration, U.S. Department of Agriculture, New Orleans, Louisiana 70179*

Synopsis

Photoinitiated, free-radical reactions of cotton cellulose with N-methylolacrylamide (NMA) from aqueous solution through direct excitation of cellulose are reported. Also reactions initiated by energy transfer from excited methyl ketone compounds to cellulose are reported. Dimethyl ketone, dimethyl ketoneformaldehyde, dimethyl diketone, dimethyl diketoneformaldehyde, methyl ethyl ketoneformaldehyde, and methyl phenyl ketoneformaldehyde were used in the sensitized reactions. When methyl ketone products were in solution during photoirradiation, they acted as sensitizers to increase the rate and extent of the reaction of NMA with cotton cellulose. When products that contained formaldehyde were covalently reacted with cotton before photoirradiation, the rate and extent of the reaction of NMA with cellulose were generally decreased. These effects can be at least partially explained by intramolecular energy transfer, as determined by chemiluminescence, electron spin resonance, and excitation fluorescence measurements. When methyl phenyl ketoneformaldehyde was covalently linked to cellulose before photoirradiation, energy localization that initiated free-radical polymerization of NMA was minimized. When cellulose that was padded with a monomer solution was dried before photoirradiation, the extent of the reaction of NMA with cellulose was decreased.

INTRODUCTION

A better understanding of photochemical processes in relation to cellulose fiber chemistry and photoinitiated polymerization reactions will help in the development of photoprocesses for selective modification of fiber properties. Two important photochemical processes in cellulose are energy absorption, transfer, and localization to excite cellulose to higher energy levels; and energy absorption to initiate reversible and irreversible reactions.^{1,2} Either of these processes can form macrocellulosic free radicals that can initiate polymerization reactions of vinyl monomers with the activated celluloses. Photoinitiated polymerization of vinyl monomers with unsensitized cellulose after direct excitation of cellulose by absorption of near-ultraviolet light has been reported.^{3,4} Also, chemical modification of cellulose to introduce benzoate groups that serve as energy sinks gave cellulosic products with improved resistance to ultraviolet light.^{5,6}

This report deals with the effects of carbonyl group-containing organic molecules such as methyl ketones on photoinitiated polymerization of N-methylolacrylamide (NMA) from aqueous solution with cellulose. The effects of ketones

* Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.

in aqueous solutions that contained NMA and of ketones covalently linked to cellulose on polymerization of NMA with cellulose are reported.

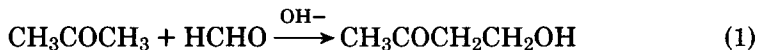
EXPERIMENTAL

Materials

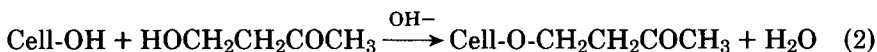
The cotton fabric, a commercial grey printcloth (0.109 kg/m², 3.15 threads/mm × 3.15 threads/mm), was desized, alkali scoured, bleached, washed with water, and air dried. Samples of the fabric were equilibrated overnight in air at about 298 K and 45% R.H. to constant weight, as previously described.^{7,8}

N-Methylolacrylamide, a commercial product in a 60% aqueous solution, was obtained without inhibitor and was used as received. Dimethyl diketone (diacetyl), methyl ethyl ketone, dimethyl ketone (acetone), methyl phenyl ketone (acetophenone), and formalin (37% formaldehyde) were obtained from commercial sources and were used as received. Other chemicals were reagent grade.

Methyl ketoneformaldehyde products were prepared by aldol condensation of ketone with formaldehyde.⁹ Typically, equimolar quantities of methyl ketone and formaldehyde from formalin solution were mixed; the pH of this solution was adjusted to about 10.5. The mixture was allowed to react at about 298 K for 58–72 ksec; then, the pH of the solution was adjusted to about 6.6. For example, the reaction of dimethyl ketone with formaldehyde under these experimental conditions was



Cotton fabrics that contained covalently linked methyl ketoneformaldehyde products were prepared by immersing the fabrics in solutions that contained the methyl ketoneformaldehyde products and sodium carbonate (about 3%) and by padding the treated fabrics to the desired wet pickup. The treated fabrics were heated at about 433 K for 240 sec. Under these conditions, reaction of the methylol group with cellulose was



Free formaldehyde and methyl ketone should be volatilized under these conditions.

Methods

The ultraviolet light source was a Rayonet photochemical reactor RPR-100 manufactured by the Southern New England Ultraviolet Company. The reactor was equipped with a set of 16 tube lamps mounted vertically around the inside walls of a cylindrical chamber (0.25 m in diameter and 0.38 m long). The reactor gave a source of radiant energy with about 85–90% of the light in the desired wavelength range. The reactor generated 21 W of ultraviolet energy at 300 nm.

Samples of fabric about 0.25 × 0.41 m were immersed in an aqueous solution

of NMA and other reagents at 298 K as indicated in the legends for the figures and then padded to the desired wet pickup by a two dip-two nip process. These treated samples, either in dried or wet pickup states, were wrapped around and fastened to cylinders made of stainless steel hardware cloth. The cylinders were about 0.41 m in circumference and 0.25 m long. These samples were placed in a quartz reactor vessel, the vessel was closed, and the atmosphere was exchanged with nitrogen. The vessel was placed in the reactor and photoirradiated with 300-nm light. The photoinitiated conversion of NMA to poly(N-methylolacrylamide) (pNMA) was more efficient with 300-nm light than with 254- or 350-nm light.^{7,8} The ambient temperature of the reactor increased from about 296 to 318 K during the initial 300 sec of photoirradiation. After the desired photoirradiation time, the samples were washed in hot water to remove unreacted monomer and chemical reagents. After the washed samples were dried, the nitrogen in the fabrics was measured by the Kjeldahl method.¹⁰ The efficiency of the conversion of NMA to pNMA add-on was calculated as (nitrogen content of modified fabric)/(nitrogen content in wet pickup).

Samples were also photolyzed by exposure to light from a PEK 110 mercury short-arc, point-source, high-pressure lamp that was operated at 100 W to determine postirradiation chemiluminescence. The electron spin resonance (ESR) spectra of free-radical intermediates formed when the samples were exposed to light were recorded as the first derivative of the absorption line at about 298 K with a Varian 4502-15 EPR spectrometer. Postirradiation chemiluminescences of photolyzed samples were measured with a Packard 3255 liquid scintillation spectrometer equipped with low dark-noise photomultiplier tubes (RCA 4501/4V) and a Packard 585 linear recorder.

The excitation and fluorescence spectra of the samples were recorded with a Farrand spectrofluorometer.

RESULTS

When dimethyl diketone was present as a photosensitizer in solution, the efficiency of the conversion of NMA to pNMA was greater than when dimethyl diketone was reacted with formaldehyde and then covalently linked to cellulose or when the sensitizer was absent (Fig. 1). When methyl ethyl ketone and methyl phenyl ketone were reacted with formaldehyde and then covalently linked to cellulose, the efficiency of photoinitiated conversion of NMA to pNMA was reduced when compared with unsensitized cellulose (Fig. 2). Covalently linked methyl phenyl ketone reduced the photoconversion of NMA to pNMA to the point that the photoinitiated polymerization reaction was inhibited.

At the low ultraviolet radiation dosages used, the efficiency of the conversion of NMA to pNMA on cellulose that was wet during photoirradiation increased as the concentration of dimethyl ketoneformaldehyde in solution increased from 0.2% to 1.0% to give a maximum efficiency of 100% (Fig. 3). If the treated cellulose was dried before photoirradiation, the efficiency of conversion of NMA to pNMA was reduced.

However, when dimethyl ketoneformaldehyde was covalently linked to cellulose, the photoinitiated conversion of NMA to pNMA was reduced, compared with unsensitized cellulose (Fig. 4). A comparison of the data reported in Figures 3 and 4, particularly the ultraviolet radiation dosages, shows that when dimethyl

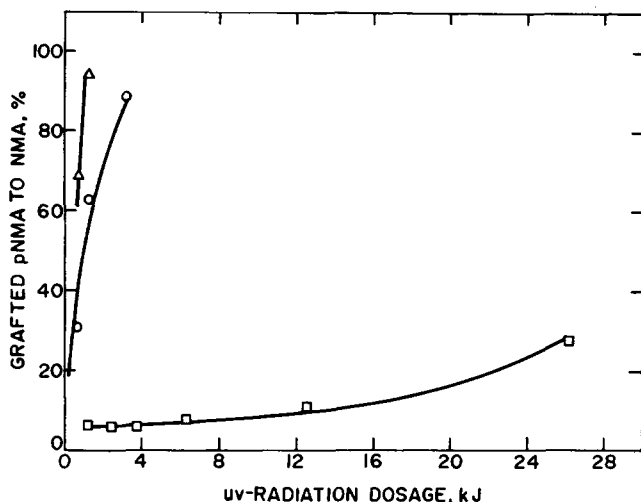


Fig. 1. Effects of dimethyl diketone on photoinitiated polymerization of N-methylolacrylamide (NMA) with cotton cellulose; cellulose padded with an aqueous solution that contained NMA (10%) to a wet pickup of about 85% by weight; irradiated in a quartz container in an atmosphere of nitrogen with 300 nm light: (Δ) cellulose + dimethyl diketone (0.043%) in padded solution; (\circ) cellulose with padded solution; (\square) cellulose-dimethyl ketoneformaldehyde (4%) with padded solution.

ketoneformaldehyde was in the solution, it gave a higher efficiency of conversion of NMA to pNMA than when covalently linked to cellulose. When formaldehyde was covalently linked to cellulose, the efficiency of conversion was reduced. When dimethyl ketone was in the solution, the efficiency of conversion was increased.

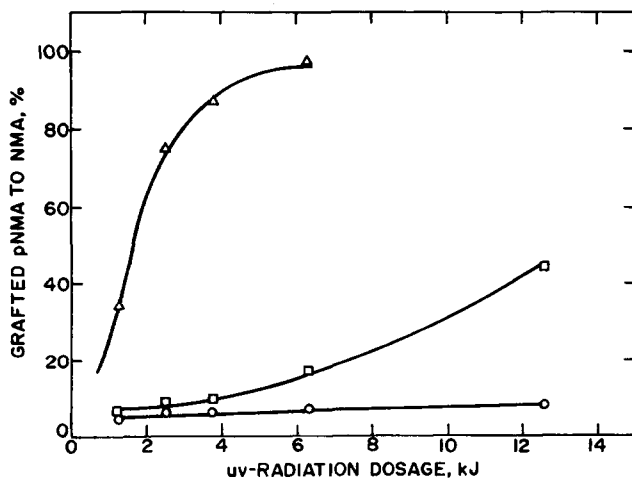


Fig. 2. Effects of methyl ethyl ketone and methyl phenyl ketone on photoinitiated polymerization of N-methylolacrylamide (NMA) with cotton cellulose; cellulose padded with an aqueous solution that contained NMA (10%) to a wet pickup of about 85% by weight; irradiated in a quartz container in an atmosphere of nitrogen with 300-nm light: (Δ) cellulose with padded solution; (\square) cellulose-methyl ethyl ketoneformaldehyde (2.4%) with padded solution; (\circ) cellulose-methyl phenyl ketoneformaldehyde (1.3%) with padded solution.

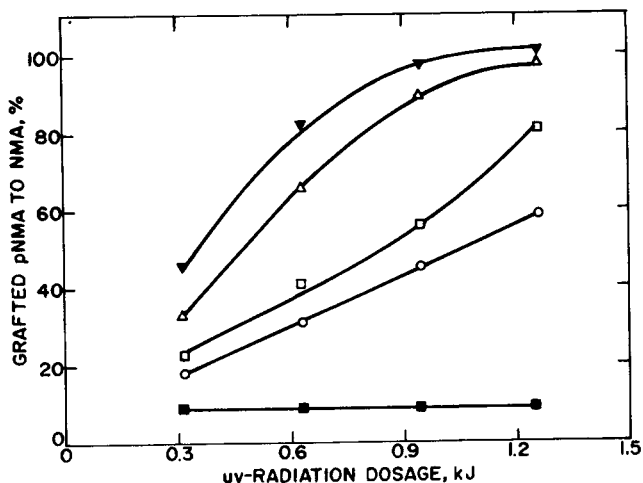


Fig. 3. Effects of dimethyl ketoneformaldehyde on photoinitiated polymerization of N-methylolacrylamide (NMA) with cotton cellulose; cellulose padded with aqueous solutions that contained NMA (10%) and dimethyl ketoneformaldehyde (0% to 1%) to a wet pickup of about 85% by weight; irradiated in a quartz container in an atmosphere of nitrogen with 300-nm light: (○) cellulose padded with solution that contained 0% dimethyl ketoneformaldehyde irradiated wet; (□) cellulose padded with solution that contained 0.2% dimethyl ketoneformaldehyde irradiated wet; (■) cellulose padded with solution that contained 0.2% dimethyl ketoneformaldehyde irradiated dry; (△) cellulose padded with solution that contained 0.5% dimethyl ketoneformaldehyde irradiated wet; (▽) cellulose padded with solution that contained 1.0% dimethyl ketoneformaldehyde irradiated wet.

ESR spectra of methyl ketone-sensitized cotton celluloses that were exposed to ambient light are shown in Figures 5 and 6. In each of these samples the methyl ketoneformaldehyde products were covalently linked to cellulose. The ESR-detectable free radical formed generated a singlet spectrum similar to that previously reported for photoirradiated cellulose² (for example, see Fig. 5). As

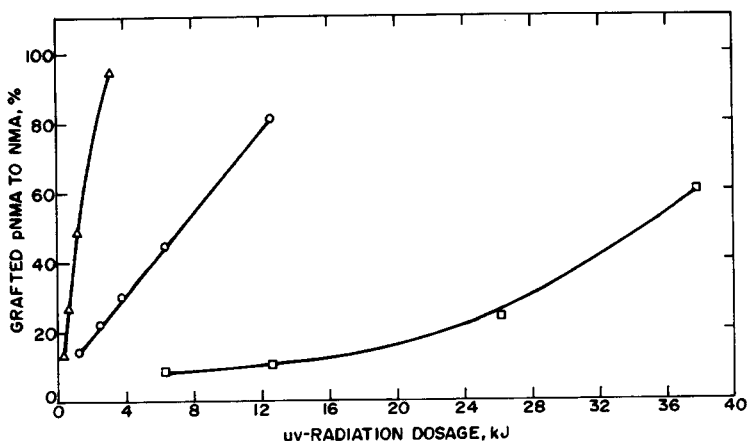


Fig. 4. Effects of dimethyl ketoneformaldehyde-cellulose on photoinitiated polymerization of N-methylolacrylamide (NMA) with cotton product; cellulose product padded with an aqueous solution that contained NMA (10%) to a wet pickup of about 85% by weight; irradiated in a quartz container in an atmosphere of nitrogen with 300-nm light: (△) cellulose with padded solution; (○) cellulose-formaldehyde (1.7%); (□) cellulose-dimethyl ketoneformaldehyde (5.4%).

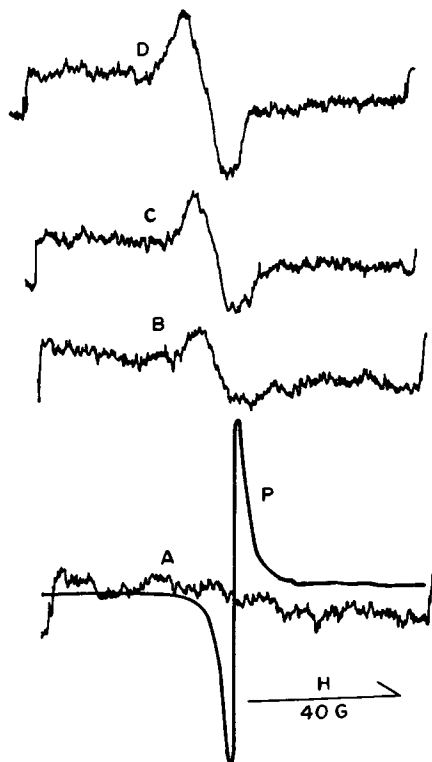


Fig. 5. Electron spin resonance spectra of dimethyl ketoneformaldehyde-cellulose exposed to light: (A) untreated cellulose; (B) cellulose-dimethyl ketoneformaldehyde (2.1%); (C) cellulose-dimethyl ketoneformaldehyde (3.6%); (D) cellulose-dimethyl ketoneformaldehyde (5.4%); (P) pitch sample marker.

the concentration of dimethyl ketoneformaldehyde increased, the relative concentrations of the macrocellulosic free radicals (proportional to the areas under the singlet spectra) increased with increased concentration of dimethyl ketoneformaldehyde.

The postirradiation chemiluminescences of cotton cellulose (curve A) and of cotton-dimethyl ketoneformaldehyde (curve B) after exposure in air to ultraviolet light are shown in Figure 7. The rate of decay in chemiluminescence was about the same for both untreated cellulose and cellulose-dimethyl ketoneformaldehyde. The count rate was greater for photoirradiated cellulose-dimethyl ketoneformaldehyde than for photoirradiated untreated cellulose.

Excitation of both untreated and all of the modified celluloses with 300 nm ultraviolet light did not generate any fluorescent peaks between 300 and 550 nm. Excitation of these celluloses with 400 nm ultraviolet light generated a fluorescent peak at about 465 nm.

DISCUSSION

Highly purified cellulose can be directly excited by the absorption of ultraviolet light and cellulosic photochemical and free-radical reactions initiated.¹⁻³ In direct excitation, macrocellulosic free radicals are formed and can initiate graft

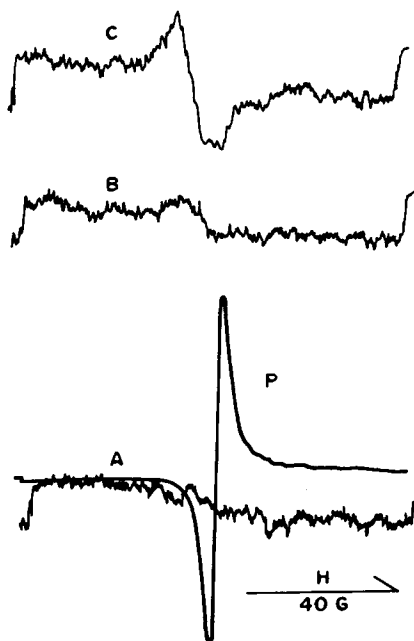
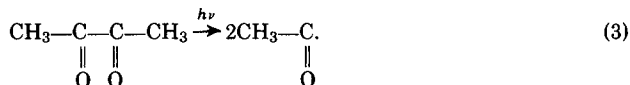


Fig. 6. Electron spin resonance spectra of ketone-modified cellulose exposed to light: (A) cellulose-methyl phenyl ketoneformaldehyde (1.3%); (B) cellulose-methyl ethyl ketoneformaldehyde (2.4%); (C) cellulose-dimethyl diketoneformaldehyde (4.0%); (P) pitch sample marker.

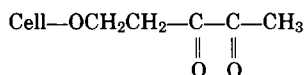
polymerization reactions with vinyl monomers.²⁻⁴ The formation and concentration of initiating free-radical species are controlled by selection of ultraviolet light wavelengths and intensities.^{2,4,7,8} Carbonyl group-containing organic molecules, such as methyl ketones, can also be used to control the formation and concentration of the initiating free-radical species.¹¹

For example, dimethyl diketone when used as a photosensitizer in solution effectively increased the efficiency of polymerization of NMA with cellulose (Fig. 1). The initiating capability as a sensitizer was principally because of Norrish cleavage I,



The excited free-radical species then reacted with the cellulosic substrate or NMA monomer, or both, to initiate polymerization.

However, when dimethyl diketoneformaldehyde was covalently linked to cellulose before irradiation to yield mainly



the formation of initiating free-radical species was decreased. See the decreased efficiency of conversion of NMA to pNMA (Fig. 1). The ESR spectrum (Fig. 6) is further evidence that light was absorbed and localized to yield a low concentration of free-radical species. Apparently, in the condensed phase in which

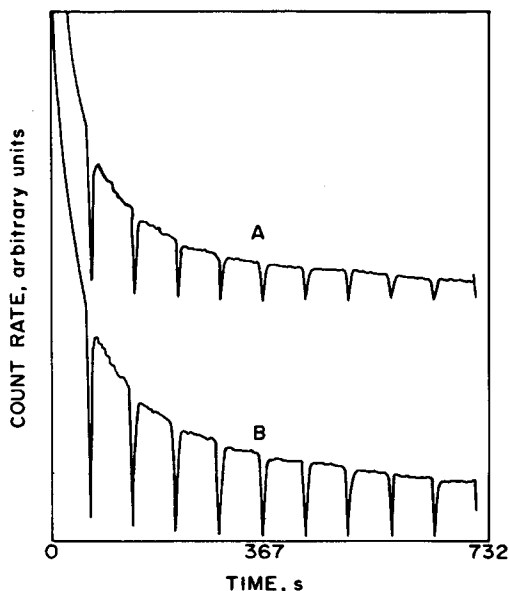


Fig. 7. Chemiluminescence of cotton cellulose after exposure in air to ultraviolet light (mercury short-arc, point-source, high-pressure, 100-W lamp) for 15 sec: (A) untreated cellulose; (B) cellulose-dimethyl ketoneformaldehyde (5.4%).

the ketone was covalently linked to cellulose polymer, fragmentation of the diketone linkage was decreased.^{11,12}

When dimethyl ketoneformaldehyde was used as a photosensitizer in solution, the efficiency of the polymerization of NMA with cellulose increased as the concentration of ketone increased (Fig. 3). If the sample was dried before photoirradiation, the conversion of NMA to pNMA was greatly reduced. Similar effects were observed when the ketone was covalently linked to cellulose (Fig. 4). ESR-detectable free radicals were formed when cellulose that contained covalently linked dimethyl ketoneformaldehyde (Fig. 5) was exposed to light. The concentration of free radicals formed was directly related to the concentration of ketone. However, in the condensed phases and dried states, these free radicals and NMA were apparently not fully accessible to initiate and maintain polymerization reactions to form pNMA. Furthermore, when cellulose that contained covalently linked dimethyl ketoneformaldehyde was excited by exposure to ultraviolet light, radiative emission of some of the absorbed energy by the excited cellulose was recorded by chemiluminescence monitoring (Fig. 7).

When methyl ethyl ketoneformaldehyde or methyl phenyl ketoneformaldehyde were covalently linked to cellulose, both the efficiency of photoconversion of NMA to pNMA (Fig. 2) and the formation of free radicals (Fig. 6) were reduced. In the condensed phase neither dialkyl ketone nor the alkyl aryl ketone was fragmented to yield initiating free-radical species.¹¹

The type of methyl ketone, wet or dried states, and condensed phases are important in determining the efficiency of photoconversion of NMA to pNMA with cellulose.

References

1. A. H. Reine and J. C. Arthur, Jr., *Text. Res. J.*, **42**, 155 (1972).
2. A. H. Reine, O. Hinojosa, and J. C. Arthur, Jr., *J. Appl. Polym. Sci.*, **17**, 3337 (1973).
3. J. C. Arthur, Jr., and O. Hinojosa, *J. Appl. Polym. Sci.*, *Appl. Polym. Symp.*, **26**, 147 (1975).
4. J. A. Harris, J. C. Arthur, Jr., and J. H. Carra, *J. Appl. Polym. Sci.*, **22**, 905 (1978).
5. J. C. Arthur, Jr., and T. Mares, U.S. Pat. 3,443,879 (1969).
6. P. J. Baugh, O. Hinojosa, T. Mares, M. J. Hoffman, and J. C. Arthur, Jr., *Text. Res. J.*, **37**, 942 (1967).
7. R. M. Reinhardt and J. C. Arthur, Jr., *J. Appl. Polym. Sci.*, **24**, 147 (1979).
8. R. M. Reinhardt, J. C. Arthur, Jr., and L. L. Muller, *J. Appl. Polym. Sci.*, **24**, 1739 (1979).
9. H. Petersen, in *Chemical Aftertreatment of Textiles*, H. Mark, N. S. Wooding, and S. M. Atlas, Eds., Wiley-Interscience, New York, 1971, p. 224.
10. Assoc. Off. Agric. Chem. Official Methods of Analysis, 12th ed., Washington, D.C., 1975, p. 15.
11. F. C. De Schryver and G. Smets, in *Reactivity, Mechanism and Structure in Polymer Chemistry*, A. D. Jenkins and A. Ledwith, Eds., Wiley-Interscience, New York, 1974, p. 446.
12. G. O. Phillips, P. Baugh, and M. Young, in *Energy Transfer in Radiation Processes*, G. O. Phillips, Ed., Elsevier, Amsterdam, 1966, p. 15.

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