

POLYCYANOACRYLATES

Introduction

Cyanoacrylate polymers are commercially important materials as structural adhesives. They combine rapid curing and high strength and are widely used to bond a diverse range of substrate surfaces, including metals, ceramics, plastics, rubbers, and biologically derived materials. The corresponding monomers were first isolated in 1947 by Ardis at B. F. Goodrich (1). Subsequently, Eastman Kodak patented them as adhesive compositions in 1957 (2) and the first commercial adhesive formulation, based on methyl 2-cyanoacrylate, was introduced in 1958 (3). Today, cyanoacrylates represent a billion dollar industry serving medical, electronic, engineering, and consumer markets worldwide. Although adhesive compositions still constitute the major segment of the business, there is growing interest and activity in the use of these polymers in other areas. These include binding agents for the controlled delivery of drugs, coatings for lithographic printing plates, waveguides for optical sensors, photoresists, and holographic recording media.

Physical Properties of Monomers

Cyanoacrylate monomers are generally low viscosity, colorless liquids that are unstable in the absence of acidic stabilizers. The commercially important materials are lower alkyl esters of 2-cyanoacrylic acid including methyl, ethyl, *n*-propyl, allyl, *n*-butyl, isobutyl, 2-methoxyethyl, 2-methoxypropyl, and *n*-octyl derivatives. The structures of some of these monomers are shown in Figure 1. The physical properties of these and related monomers are reported in detail in several previous

Table 1. Properties of Some Common Cyanoacrylate Monomers^a

	Methyl	Ethyl	Isopropyl	Allyl	<i>n</i> -Butyl	2-Methoxyethyl
Boiling point, °C	85–86	92–93	109–112	120–122	118–120	136–138
at kPa ^{b,c}	1.5	1.3	1.6	1.6	1.1	0.1
Viscosity at 25°C, mPa·s(=cP)	2	2	2	2	2	3
Density, g/cm ³	1.10	1.05	1.01	1.05	0.98	1.06
Refractive index n_{20}^D	1.44	1.43	1.43	1.46	1.43	1.43 ^d
Flash point, °C	83	83	–	82	85	–
Surface tension ^b at 30°C, mN/m (=dyn/cm)	44.5	38.8	34.5	39.5	34.2	41.5
Lap-shear adhesive strength, MPa ^{e,f}	22.0	17.2	20.9g	21.5	15.7	18.6

^aData from Ref. 3 unless otherwise indicated.

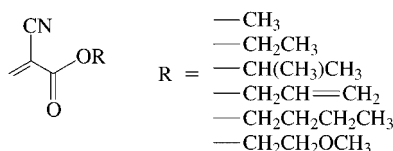
^bData from Ref. 5.

^cTo convert kPa to mm Hg, multiply by 7.5.

^d n_{D30} from Ref. 5.

^eASTM D1002, steel substrates.

^fTo convert MPa to psi, multiply by 145.

**Fig. 1.** Some commercially important cyanoacrylate monomers.

publications (3–5). A summary of the bulk physical properties of some common monomers is presented in Table 1.

The lower esters of alkyl 2-cyanoacrylates (eg, methyl, ethyl esters) provide adhesives with excellent lap-shear strengths to a variety of different substrates (3). They are, however, brittle materials and generally require the addition of a rubber-toughening agent to improve peel strength and impact resistance (4). The low esters have pungent odors whereas the higher esters, in particular the alkoxyalkyl esters, are virtually odorless (3).

Chemical Properties of Monomers

The chemical properties of cyanoacrylate monomers are primarily determined by the highly electron-deficient nature of the alkene double bond. In the presence of catalytic amounts of basic or nucleophilic species they undergo rapid anionic bulk polymerization reaction and this chemistry is discussed in more detail later. Under neutral or acidic conditions, cyanoacrylates are good dienophiles and readily undergo [4+2] cycloaddition reactions with conjugated dienes such as butadiene or anthracene (6,7). However, in the presence of stoichiometric quantities of electron-rich monomers, such as vinyl ethers, they undergo heterodiene cycloadditions to give substituted dihydropyrans (8) (Fig. 2). The diene adducts

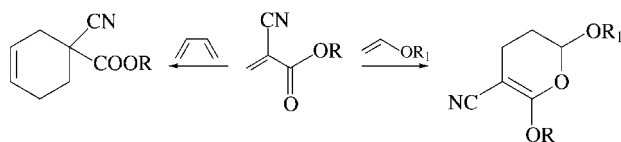


Fig. 2. Cycloaddition reactions of cyanoacrylates.

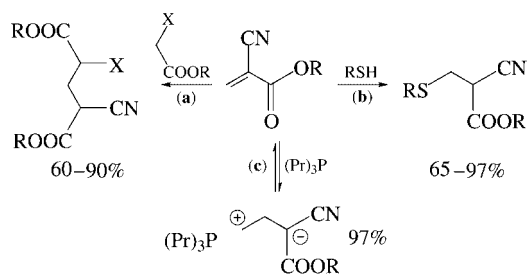


Fig. 3. Michael-type addition reactions to cyanoacrylates: (a) 5% piperidine, acetonitrile, 20°C, X = NO₂, CN, COR; (b) acetone, 3.5 h, 20°C, R = CH₂COOH, C₂H₄SH; (c) dry benzene, 3 h, 20°C.

are stable and are frequently used to characterize the more reactive monomers. In contrast, the dihydropyrans are unstable and are readily isomerized or polymerized (8,9).

Cyanoacrylates may also add to a variety of organic acids in piperidine-catalyzed Michael-type reactions (10–12). Thus nitro-, cyano-, and acetoacetates give the corresponding glutarate derivatives in moderate to high yields (Fig. 3a). However, as the acidity of the organic acid decreases, the yield of Michael adduct decreases and polymerization predominates. From a synthetic viewpoint the reaction is useful only for acids having $pK_a < 13$. Similarly, thiols and thiocarboxylic acids add to cyanoacrylate monomers to give the corresponding β -thioethers in high yields (11,12). This reaction proceeds at room temperature and does not require a catalyst (Fig. 3b). However, slow addition of monomer to thiol is required to ensure that polymerization does not occur. Similar techniques are used to prepare internal zwitterionic salts of cyanoacrylates and trialkylphosphines (Fig. 3c) (10,11,13). The salts are stable over several months, provided they are stored under anhydrous conditions.

Manufacture of Monomer

Cyanoacrylate monomers are usually prepared by a base-catalyzed Knoevenagel condensation of alkyl cyanoacetate and formaldehyde to give an intermediate low molar mass polymer which is then depolymerized under acidic conditions at elevated temperatures (14–17). Figure 4 depicts the process for the production of methyl 2-cyanoacrylate.

The condensation step is preferably carried out with paraformaldehyde in the presence of a nonaqueous solvent to facilitate the removal of water by azeotropic distillation (15). The reagents are generally employed in stoichiometric amounts,

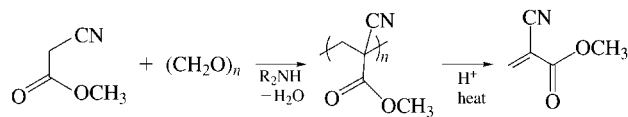


Fig. 4. Synthetic route for production of methyl 2-cyanoacrylate.

although a small excess of cyanoacetate may be employed to reduce the viscosity of the intermediate polymer solution, thus improving its processing characteristics (16). On completion of the condensation step, the solvent is removed and the oligomer treated with anhydrous acid, such as P_2O_5 , to neutralize the catalyst and remove traces of residual water. The depolymerization reaction is carried out under reduced pressure at temperatures in the range $150\text{--}250^\circ\text{C}$ and is facilitated by the addition of a nonreactive heat transfer medium, such as tricresyl phosphate (15). Acidic vapor-phase stabilizers, such as SO_2 , and free-radical inhibitors, such as 1,4-hydroquinone, are also added to ensure stability of the monomer as soon as it is formed (15,16). On heating, the polymer decomposes to produce monomer vapor, which is passed through a distillation condenser and collected as a liquid. The crude monomer obtained in this way is then purified by redistillation and carefully stabilized with low levels of acidic inhibitors (18).

Other methods for the synthesis of cyanoacrylate monomers include pyrolysis of 3-alkoxy-2-cyanopropionates (1), transesterification of cyanoacrylates with alcohols (19,20), displacement of monomer from the corresponding anthracene Diels–Alder adduct by treatment with maleic anhydride (7,21), esterification of cyanoacrylic acid or cyanoacryloyl chloride with alcohols (22), and the oxidation of alkyl 2-cyanopropionate phenyl selenides with hydrogen peroxide (23). These alternative methods are particularly useful for the preparation of monomers not readily prepared by thermal decomposition of cyanoacrylate polymer.

Polymerization

Cyanoacrylate monomers undergo extremely rapid polymerization in the presence of catalytic amounts of anionic initiators or certain covalent bases such as tertiary amines and phosphines. The reaction is completely inhibited by strong acids and is thus anionic in nature. The kinetics of base-catalyzed solution polymerization has been studied in detail utilizing adiabatic calorimetry (24–35). These studies show that in the absence of strong acid the polymerization has no intrinsic termination reaction. The overall kinetics depends on the rate of initiation and may be distinguished between those reactions in which initiators exhibit very rapid rates of initiation (eg, hydroxyl ions or phosphines) and those where the initiation sequences are relatively slow (eg, acyclic amines or pyridine). With rapid initiators, nearly ideal living polymerization conditions exist and molecular weights are in close approximation to the theoretical values from the monomer/initiator ratios employed (25). For such cases a classical anionic polymerization mechanism is postulated (Fig. 5). With covalent bases such as tertiary amines, the initiation step involves one or more reversible monomer addition reactions before the propagation sequence becomes established and the polymerization proceeds via a zwitterionic mechanism (29,30).

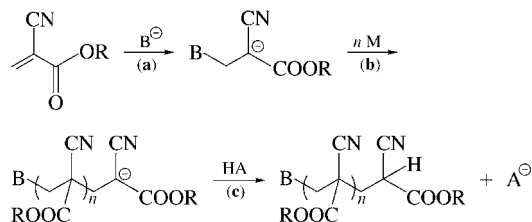


Fig. 5. Base (B)-catalyzed anionic polymerization mechanism of cyanoacrylate monomer (M): (a) initiation, (b) propagation, and (c) transfer/termination by acid (HA).

Although cyanoacrylate polymers are most commonly prepared by anionic polymerization, they may also be prepared by free-radical polymerization using conventional radical initiators (36–38), provided adequate amounts of anionic polymerization inhibitors are employed. Bulk photoanionic polymerization of cyanoacrylates has also been described by a number of workers (39–43). These systems rely on the *in situ* generation of an anionic initiator from a neutral species, following absorption of light of an appropriate wavelength. The zwitterionic and radical copolymerization of cyanoacrylates has also been reported for a number of comonomers including vinyl ethers (44), ketene acetals (45), furan (46), vinyl ketones (47), and ethylene (48).

Properties of Polymers

The physical properties of poly(alkyl 2-cyanoacrylates) are discussed in a recent review (49). The polymers are colorless and amorphous solids that readily undergo retropolymerization reactions at temperatures in the region 140–180°C (50). Glass-transition temperatures T_g vary depending on the method of measurement, conditions of synthesis, etc, with values typically in the range of –78 to +165°C (*n*-decyl and methyl cyanoacrylate polymers respectively). The solubility of methyl, ethyl, and *n*-butyl cyanoacrylate polymers were systematically determined in a wide range of common solvents (51). The polymers are generally soluble in polar aprotic solvents (eg, DMSO, DMF) and insoluble in both nonpolar solvents (eg, hexane, ether) and polar solvents (eg, methanol, water). Solubility improves as the size of the alkyl group increases. Intrinsic viscosities $[\eta]$ of ethyl and *n*-butyl cyanoacrylate polymers have been measured in a number of different solvents and found to give linear log–log relationships with number-average molecular weight M_n over approximately 2 orders of molecular weight range. The Mark–Houwink constants were determined and found to be internally self-consistent for a range of different solvents (51).

The thermodynamic properties of several cyanoacrylate polymers have been determined using precision adiabatic and isothermal calorimetry (52–55). The Gibbs free energy ΔG_0 estimated from the enthalpy ΔH_0 and entropy ΔS_0 of the bulk polymerization of various monomers showed that polymerization is thermodynamically feasible over the temperature range –270 to +160°C at standard pressure. Ceiling temperatures T_c for polymerization were derived from the thermodynamic data and represent the upper temperature limit of polymerization.

Table 2. Thermodynamic Parameters for Some Cyanoacrylate Polymerizations at 25°C and Atmosphere Pressure (101.3 kPa)

Parameter ^a	Ethyl	Allyl	<i>N</i> -Decyl
$-\Delta H_0$, kJ/mol	48	64	69
$-\Delta S_0$, J/mol·K	88	85	141
$-\Delta G_0$, kJ/mol	21	39	39
T_c , °C	267	307	217
T_g , °C	149	122	-78
Ref.	55	52	53

^aTo convert J to cal, divide by 4.184.

Glass transitions (T_g) were obtained from plots of heat capacity with temperature and clearly show a decrease in value as the size of the alkyl side chain increases. Typical data are presented in Table 2..

Cyanoacrylate polymers are also rapidly degraded in solution at temperatures substantially below T_c in the presence of basic species (56,57). Size exclusion chromatography showed that an initial high molecular solution of unimodal polycyanoacrylate degrades over 60s at ambient temperature to produce a lower molecular weight distribution following the addition of a catalytic amount of hydroxide ion. This degradation was attributed to a chain-end unzipping of monomer followed by its immediate repolymerization to produce an intermediate bimodal distribution of molecular weights.

Dynamical mechanical analyses are reported for a range of solvent cast films of cyanoacrylate polymers ranging in molecular weight from 75,000 to 330,000 (58). The storage moduli decrease with increasing size of the alkyl side chain and generally fall off sharply at temperatures above T_g . An exception to this trend is poly(allyl 2-cyanoacrylate), which exhibits an increase in modulus that is attributed to cross-linking through the unsaturated side group. Refractive indices of cyanoacrylate polymers are in the range 1.45–1.48 and dielectric constants vary from 3.3 to 5.4 at 1 MHz (3).

Economic Aspects

The principal manufacturers and suppliers of cyanoacrylate monomers include Henkel (Loctite Div.), National Starch, Toagosei, Sumitomo, and Three-bond. The largest market for these materials is in the formulation of so-called *instant adhesives* for which the U.S. production is now estimated in the region 2000 t annually. Although this represents a relatively small fraction of the total volume of adhesives business, it corresponds to a disproportionately high value due to the high costs of cyanoacrylate monomers.

Specifications and Standards

Cyanoacrylates are generally specified in relation to their intended end use (see section on Uses). For adhesives this will usually include details of the physical properties of uncured formulations (eg, viscosity, density, flash point), curing

performance and conditions in a standard joint configuration (cure time, effect of humidity, etc) and a variety of physical, chemical, and materials performance properties (T_g , adhesive strength, durability, chemical resistance etc). These data are generally available in technical product bulletins provided by the manufacturers and suppliers of the various monomers.

Analytical and Test Methods

Cyanoacrylate monomers and polymers are routinely characterized by all common chromatographic and spectroscopic techniques including ir, nmr, ms, gc, sec, and uv analytical techniques. The levels of acid stabilizers in monomers are usually determined by potentiometric titration. Microstructural assignments of anionically and zwitterionically polymerized poly(ethyl 2-cyanoacrylate) have been unambiguously determined using DEPT and ^1H - ^{13}C HETCOR nmr analysis (59).

Health and Safety Factors

Volatile cyanoacrylate monomers, in particular methyl and ethyl cyanoacrylates, have characteristic acrid odors. Exposure to these materials at levels in the range of 1–5 ppm results in irritation to the eyes, nose, and throat (3). It is recommended that these monomers be used in a well-ventilated area, that skin and eye contact be avoided, and that the user be familiar with the relevant safety data supplied by product manufacturers. A recent epidemiological study in workers with occupational exposure to monomer vapors concluded that there was no increased risk of pulmonary obstruction (eg, asthma) on exposure to average short-time concentrations of less than 0.5 ppm (60). Polymerization of cyanoacrylates is rapid and exothermic and particular care should be taken to avoid burns, which can result from the unexpected bulk polymerization of inadequately stabilized or contaminated monomer samples.

Uses

Adhesives represent by far the most important use of cyanoacrylates. They are marketed throughout the world for both industrial and consumer use. They polymerize rapidly on contact with many surfaces and exhibit excellent adhesive strength to a wide variety of different materials. The beneficial adhesive properties are attributed to a combination of good wetting of surfaces by the monomers, the high polarity of the polymer, and the high molecular weight of the bulk polymer, which is frequently in excess of 10^6 . The typical adhesive product comprises a mixture of monomers, stabilizers, and additives (such as thickeners, rubbers, fillers) to control the rheology of the uncured composition and properties of the cured adhesive. Several comprehensive reviews on cyanoacrylate adhesives have been published (3,4).

Traditionally cyanoacrylates have been used to facilitate the automated assembly of various devices and components including computers, calculators, electric motors, medical equipment, optical components, jewelry, and sporting

goods. More recently, cyanoacrylate adhesives are being used in surgical areas such as tissue adhesives for wound closure (61), sealing corneal perforations (62), and for the control of gastrointestinal bleeding (63). Cyanoacrylate adhesives are associated with a comparatively low incidence of post-operative infection and the cured polymers are generally considered to be biodegradable, biocompatible, non-toxic, and nonallergenic (61,63). Cyanoacrylate esters with higher alkyl group side chains (eg, *n*-butyl, *n*-octyl) are preferred for surgical applications, as they have been shown to be less toxic to surrounding tissues (62).

Cyanoacrylate polymers are also extensively used in the production of encapsulated colloidal nanoparticles for targeted drug delivery systems and are particularly useful in the treatment of certain cancers (64). Their good encapsulation properties, low toxicity, and satisfactory biocompatibility make them attractive for this application. By forming amphiphilic copolymers of cyanoacrylate and ethylene oxide, the therapeutic activity of entrapped compounds can be enhanced. The copolymer functions to prolong the circulation lifetime of the nanoparticles after they have been introduced into the bloodstream (65).

Other potential uses of cyanoacrylate polymers include the development and characterization of latent fingerprints by vapor-phase deposition of polymer (66) and the deposition and growth of plasma-resistant photoresist films by interfacial polymerization from the vapor phase (67). Potential applications in the optical area include the formation of high tilt angle alignment layers in liquid crystal devices (68), the production of holographic media for optical data storage (69), and the production of waveguide sensors for the detection of organic vapors (70). Polycyanoacrylate films containing infrared dyes are readily ablated on exposure to laser light and may be used to produce lithographic printing plates with good ink receptivity, adhesion, and wear resistance (71).

BIBLIOGRAPHY

- “2-Cyanoacrylic Ester Polymers” in *EPST* 1st ed., Vol. 1, pp. 337–342, by H. W. Coover Jr. and T. H. Wicker Jr., Tennessee Eastman Co., a division of Eastman Kodak Co., “Acrylic and Methacrylic Ester Polymers, 2-Cyanoacrylic Ester Polymers” in *EPSE* 2nd ed., Vol. 1, pp. 299–305, by H. W. Coover Jr. and J. M. McIntire, Eastman Kodak Co.
1. U.S. Pat. 2467926 (1947), A. E. Ardis (to The B.F. Goodrich Co.).
 2. U.S. Pat. 2794788 (1957), H. W. Coover and N. H. Shearer (to Eastman Kodak Co.).
 3. H. W. Coover, D. W. Dreifus, and J. T. O'Connor, in I. Skeist, ed., *Handbook of Adhesives*, 3rd ed., Van Nostrand Reinhold, Co., Inc., New York, 1990, pp. 463–477.
 4. G. H. Millet, in S. R. Hartshorn, ed., *Structural Adhesives, Chemistry and Technology*, Plenum Press, New York, 1986, pp. 249–307.
 5. V. Vijayalakshmi, J. N. Vani, and N. Krishnamurti, *J. Adhes. Sci. Technol.* **4**, 733 (1990).
 6. U.S. Pat. 2467927 (1947), A. E. Ardis (to The B. F. Goodrich Co.).
 7. U.S. Pat. 4012402 (1977), C. J. Buck (to Johnson & Johnson).
 8. H. A. Rasoul and H. K. Hall, *J. Org. Chem.* **47**, 2080 (1982).
 9. I. Cho and J.-Y. Lee, *Macromolecules* **16** 1245 (1983)
 10. Y. G. Gololobov, G. D. Kolomnikova, and T. O. Krylova, *Russ. J. General Chem.* **64**, 373 (1994).
 11. Y. G. Gololobov and T. O. Krylova, *Heteroat. Chem.* **6** 271 (1995).
 12. I. I. Kandror and co-workers, *Izv. Akad. Nauk. SSSR, Ser. Khim.* (12), 2816 (1991).

13. T. O. Krylova and co-workers, *Russ. J. General Chem.* **64**, 371 (1994).
14. U.S. Pat. 2467927 (1947), A. E. Ardis (to B. F. Goodrich Co.).
15. U.S. Pat. 2721858 (1955), F. B. Joyner and G. F. Hawkins (to Eastman Kodak Co.).
16. U.S. Pat. 3254111 (1966), G. F. Hawkins and H. F. McCurry (to Eastman Kodak Co.).
17. J. M. Rooney, *Polym. J.* **13**, 975 (1981).
18. U.S. Pat. 2794788 (1957), H. W. Coover and N. H. Shearer (to Eastman Kodak Co.).
19. Russ. Pat. SU 726086 (1980), J. Voitekunas and co-workers (to USSR Academy of Sciences).
20. U.S. Patent 6096848 (2000), Y. Gololobov, W. Gruber, and C. Nicolaisen (to Henkel).
21. L. Giral and co-workers, *Ann Pharm. Fr.* **43**, 439 (1960).
22. PCT Pat. Application WO 9415907 (1994), V. A. Dyatlov and G. A. Katz (to Eurotax Ltd.).
23. P. Klemarczyk, *Polymer* **39** (1), 173 (1998).
24. E. F. Donnelly and co-workers, *J. Polym. Sci. Polym. Lett.* **15**, 399 (1977).
25. D. C. Pepper, *J. Polym. Sci., Polym. Symp.* **62**, 65 (1978).
26. D. C. Pepper, *Polym. J. (Tokyo)* **12**, 629 (1980).
27. D. S. Johnston and D. C. Pepper, *Makromol. Chem.* **182**, 393 (1981).
28. D. S. Johnston and D. C. Pepper, *Makromol. Chem.* **182**, 407 (1981).
29. D. S. Johnston and D. C. Pepper, *Makromol. Chem.* **182**, 421 (1981).
30. D. C. Pepper and B. Ryan, *Makromol. Chem.* **184**, 383 (1983).
31. D. C. Pepper and B. Ryan, *Makromol. Chem.* **184**, 395 (1983).
32. D. C. Pepper, *Makromol. Chem.* **188**, 527 (1987).
33. J. P. Cronin and D. C. Pepper, *Makromol. Chem.* **189**, 85 (1988).
34. I. C. Eromosele and D. C. Pepper, *Makromol. Chem.* **190**, 3085 (1989).
35. I. C. Eromosele and D. C. Pepper, *Makromol. Chem.* **190**, 3095 (1989).
36. A. J. Canale and co-workers, *J. Appl. Polym. Sci.* **4**, 231 (1960).
37. J. C. Bevington and J. A. Jemmett, *J. Chem. Soc., Faraday Trans.* **69**, 1866 (1977).
38. B. Bunichiro, M. Yoshioka, and T. Otsu, *Makromol. Chem.* **184**, 1025 (1983).
39. C. Kotal, P. A. Grutsch, and D. B. Yang, *Macromolecules* **24**, 6872 (1991).
40. B. J. Palmer and co-workers, *Macromolecules* **28**, 1328 (1995).
41. N. Arsu, A. Onen, and Y. Yagci, *Macromolecules*, **29**, 8973 (1996).
42. R. B. Paul and co-workers, *Polymer* **38**, 2011, (1997).
43. Y. Yamaguchi and co-workers, *Macromolecules* **31**, 5155 (1998).
44. H. A. Rasoul and H. K. Hall Jr., *J. Org. Chem.* **47**, 2080, (1982).
45. T. Yokozawa, K. D. Ando, and T. Endo, *Macromolecules* **27**, 1978 (1994).
46. E. Oikawa, F. Aoki, and K. Katano, *Polym. J.* **11**, 257 (1997).
47. K. Maruyama and co-workers, *Int. J. Adhesn. Adhesv.* **9** (3), 143 (1989).
48. C. D. Eisenbach, W. Liebert, and B. Sperlich, *Angew. Makromol. Chem.* **223**, 81 (1994).
49. J. Woods, in J. C. Salamone, ed., *Polymeric Materials Encyclopedia*, Vol. **2**, CRC Press, Inc., Boca Raton, 1996, p. 1632.
50. J. M. Rooney, *Br. Polym. J.* **13**, 160, (1981).
51. E. F. Donnelly and D. C. Pepper, *Makromol. Chem., Rapid Commun.* **2**, 439 (1981).
52. E. G. Kiparisova and co-workers, *Polym. Sci.* **35**, 743 (1993).
53. T. A. Bykova and co-workers, *Polym. Sci.* **35**(1), 8 (1993).
54. T. A. Bykova and co-workers, *Polym. Sci.* **33**, 2453 (1991).
55. T. A. Bykova and co-workers, *Polym. Sci.* **33**, 537 (1991).
56. B. Ryan and G. McCann, *Makromol. Rapid Commun.* **17**, 217 (1996).
57. D. R. Robello, T. D. Eldridge, and M. T. Swanson, *J. Polym. Sci. Part A* **37**, 4570 (1999).
58. K. H. Cheung and co-workers, *Makromol. Chem.* **188**, 3041 (1987).
59. D. R. Robello, T. D. Eldridge, and F. M. Michaels, *J. Polym. Sci. Part A* **37**, 2219 (1999).
60. M. Goodman and co-workers, *J. Toxicol. Environ. Health, Part A* **59**, 135 (2000).
61. R. Vanholder and co-workers, *Biomaterials*, **14**, 737 (1993).

62. G. R. John in T. J. Zimmerman, ed., *Textbook of Ocular Pharmacology*, Lippincott-Raven, Pa, 1977, p. 671.
63. D. Katti and N. Krishnamurti, *J. Appl. Polym. Sci.* **74**, 336 (1999).
64. F. Lescure and co-workers, *J. Colloid Interface Sci.* **154** (1), 77 (1992).
65. M. T. Peracchia and co-workers, *Pharm. Res.* **15**, 550 (1998).
66. D. T. Burns and co-workers, *Anal. Chim. Acta* **362**, 171 (1998).
67. J. Woods and co-workers, *Polymer* **30**, 1091 (1989).
68. C. B. McArdle and J. Woods, in K. L. Mittal and K.-W. Lee, eds., *Polymer Surfaces and Interfaces*, VSP Publishers, Utrecht, the Netherlands, 1997, p. 225.
69. R. A. Rupp and co-workers, *Polymer* **38**, 2299 (1997).
70. R. P. Podgorsek and co-workers, *Sensors and Actuators B* **51**, 146, (1998).
71. U.S. Pat. 5605780 (1996), M. S. Burberry, C. D. DeBoer and S. W. Weber (to Eastman Kodak Co.).

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POLYDIACETYLENE. See DIACETYLENE AND TRIACETYLENE POLYME.