noacetamido]-3-(3-bromotetrahydrofuran-2-vl)-3-cephem-4-carboxylate (10). To a suspension of PCI₅ (0.64 g. 3.0 mmol) in CH₂Cl₂ at the ice-bath temperature was added pyridine (0.24 g, 3.0 mmol). The mixture was stirred at the same temperature for 10 minutes before addition of 8 (1.47 g, 2.8 mmol). After treated with 2 hours at -10° C the reaction mixture was carefully MeOH (30 ml) at -30°C. The resulting mixture was stirred at 0°C and concentrated under reduced pressure. The residue was pulverized with diethyl ether to give 0.87 g (70%) of 9. Compound 9 was used in the subsequent reaction without further purification. To a solution of 2-(2-aminothiazole-4-yl)-2-methoxyiminoacetic acid (0.50 g. 2.5 mmol) and 1-methanesulfonyloxy-6-trifluoromethylbenzotriazole (FMS, 0.65 g, 2.3 mmol) in DMF (15 ml) at 0°C was added triethylamine (0.25 g. 2.5 mmol) and 9 (0.87 g. 2 mmol). After stirring at room temperature for 2 hours, the reaction mixture was poured into a mixture of EtOAc (100 ml) and aq NaHCO3. The separated EtOAc layer was washed with brine, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residue was triturated with n-hexane to give 0.78 g (67%) of 10 as a powder: IR(KBr) cm⁻¹ 1782 (β-lactam C=0); ¹H-NMR (CDCl₃) δ 1.50 (9H, bs, t-butyl), 2.42, 2.65 (2H, m, 4-H tetrahydrofuran ring), 3.54, 3.88 (2H, ABq, 2-H, J = 18 Hz), 4.06 (3H, s, -OCH₃), 4.04, 4.25 (2H, m, 3-H, 5-H tetrahydrofuran ring), 5.08 (1H, d, 6-H, J=5 Hz), 5.15, 5.25 (2H, m, 2-H, 5-H tetrahydrofuran ring), 6.00 (1H, dd, 7-H, J=5 Hz, 9 Hz), 6.95 (1H, s, aminothiazol-H), 7.05 (1H, d, NH, J=9 Hz).

7-[(Z)-2-(2-Aminothiazol-4-yl)-2-methoxyiminoace-tamido]-3-(3-bromotetrahydrofuran-2-yl)-3-cephem-4-carboxylic acid (11). A mixture of 10 (0.59 g, 1 mmol), trifluoroacetic acid (5 ml) and anisole (5 ml) in CH_2Cl_2 (30 ml) was stirred at $-10^{\circ}C$ for 30 minutes and at room temperature for 4 hours, and concentrated under reduced pressure. The residue was triturated with diethyl ether to give 0.30 g (56%) of 11 as a crude product, which was purified by column chromatography on silica gel using CH_3CN -MeOH, 4:1, as eluent. 52 mg (10%) of 11 as a solid: mp. 150-151 $^{\circ}C$ (dec.); IR(KBr) cm⁻¹ 1778 (β -lactam C=O); ¹H-NMR (DMSO-d₀) δ 2.30, 2.70 (2H, m, 4-H tetrahydrofuran ring),

3.80 (3H, s, OCH₃), 3.62, 3.80, 3.95, 4.15 (4H, m, 3-H, 5-H tetrahydrofuran ring and 2-H), 4.95 (1H, d, 6-H), 5.05, 5.18 (2H, m, 2-H, 5-H tetrahydrofuran ring), 5.78 (1H, dd, 7-H), 6.70 (1H, s, aminothiazol-H), 7.25 (2H, bs, NH₂), 9.70 (1H, d, NH).

References

- 1. R. Scartazzini and H. Bickel, Heterocycles, 7, 1165 (1977).
- R. R. Chauvette and P. A. Pennington, J. Med. Chem., 18, 403 (1975).
- D. Ikeda, S.-P. Huang, Y. Koyama, M. Hamada, S. Kondo and T. Takeuchi, in: Program, and Abstracts of the 30th Interscience Conference on Antimicrobial Agents and Chemotherapy, Atlanta, Georgia. Abstr. 458 (1990).
- K. F. Bernady, M. B. Floyd, J. F. Poletto, and M. J. Weiss, J. Org. Chem., 44, 1438 (1979).
- G. Piancatelli, A. Scettri, and M. D'Auria, Synthesis, 245 (1982).
- (a) H. Yamanaka, T. Chiba, K. Kawabata, H. Takasugi, T. Masugi, and T. Takaya, J. Antibiotics, 38, 1738 (1985);
 (b) T. Takaya, H. Takasugi, T. Masugi, H. Yamanaka, and K. Kawabata, US Patent 4,423,213,27 December (1983).
- (a) H. Peter, B. Mueller, and H. Bickel, Helv. Chim. Acta.,
 58, 2450 (1975); (b) A. H. Shingler and N. G. Weir, in: Recent Advances in the Chemistry of β-Lactam Antibiotics, ed. J. Elks, The Chemical Society, London, 153 (1977).
- T. Naito, H. Hoshi, S. Aburaki, Y. Abe, J. Okumura, K. Tomatsu, and H. Kawaguchi, J. Antibiotics, 40, 991 (1987).
- M. Miyashita, A. Yoshikoshi, and P. A. Grieco, J. Org. Chem., 42, 3772 (1977).
- (a) S. J. Rhoads and J. M. Watson, J. Amer. Chem. Soc.,
 93, 5813 (1971); (b) A. B. Reitz, S. O. Nortey, and B. E. Maryanoff, J. Org. Chem., 52, 4191 (1987).
- H. Guenther, in: NMR-Spektroskopie, Georg Thieme, Stuttgart, 105-107 (1983).
- C. H. Lee, C. J. Moon, K. S. Kim, J. H. Kim, and D. W. Kim, Bull. Korean Chem. Soc., 8, 336 (1987).

The Gelation Studies, of N-Methylolated PAAms in Aqueous Media

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The gelation phenomena of N-methylolated PAAm (M-PAAm) in aqueous media was studied. The critical gelation concentration (CGC) was very close to the calculated C* of the scaling theory. But the CGC of lower MW M-PAAm deviated from C* due to contamination of small molecules. We propose that the CGC is the close packing configuration of polymer molecules in solution. The experimental results of the gelation of M-PAAm/PAAm mixture proved that the close packing configuration is essential to make a gel. We calculated the minimum quantity of M-PAAm to make M-PAAm/PAAm mixture a gel by using the close packing configuration. We used a lattice model.

Introduction

Gelation is needed to make crosslinked polymers, which

have many important uses in polymer and other fields of science. The method of gelation is divided into two. One is the most popular one step copolymerization of monomer