PII: S0032-3861(97)10385-8

# Cellulose methacrylate: synthesis and liquid crystalline behaviour of solutions and gels

## Enrico Marsano*, Luigi De Paz, Ennio Tambuscio and Estella Bianchi
*Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso 31, 16146 Genova, Italy*

A new derivative of cellulose was synthesized by reaction of the polymer dissolved in dimethylacetamide (DMAc)/5% LiCl and methacryloyl chloride. The control of the molar ratio between the reagents and the temperature permits one to obtain a specific degree of substitution (DS). Cellulose methacrylate (CEMA) is a semirigid polymer with a persistence length which decreases as the DS increases. Consequently, the polymer concentration $C_p$ at which the anisotropic phase becomes stable gets higher as the DS increases. CEMA solutions gellify when irradiated by UV, due to the crosslinking reaction of lateral double bonds. Swelling in DMAc/5% LiCl and water depends on the CEMA concentration and irradiation time. The first appearance of optical anisotropy may be observed at a polymer critical concentration which is always lower than the $C_p'$ of the uncrosslinked polymer. © 1998 Elsevier Science Ltd. All rights reserved.

## INTRODUCTION

Networks based on semirigid polymers are nowadays considered as rather interesting systems because of their peculiar behaviour. The capability to give liquid crystalline mesophases in solutions or melts, characteristic of semirigid polymers, generally extends to their gels. High degrees of segmental orientation and isotropic to nematic transition may be observed experimentally under strain and (or) by changing the swelling degree of the network[1,2]. Moreover, even the elastic behaviours are quite different from those of classical rubbery systems.

From a chemical point of view, the majority of polymers involved in these kinds of network owe their rigidity to the presence of an aromatic or ring structure along the chain, characterized by large rotational barriers or by intramolecular hydrogen bonds which hamper internal rotation. Gels based on semirigid polymers have been extensively studied in recent years[1–9]. The use of polysaccharidic materials appears to be of specific interest when the swelling behaviour of gels in organic polar solvent or water is added to their mesogenic properties.

In a previous paper[3] we studied the behaviour of organogels based on cellulose (CE), showing liquid crystalline order. Starting from a solution of the polymer in dimethylacetamide containing 4% (w/w) LiCl (DMAc/4%LiCl), two routes were followed to perform the crosslinking process. The first one makes use of a bifunctional unit (adipoyl chloride): the crosslinking degree increases by increasing the ratio between the crosslinker and the polymer, with a significant variation of the chemical composition. This may have a strong influence on the swelling in different solvents: the expected decreasing trend of swelling with the increase of crosslinking may be completely inverted in a specific solvent, opening the way to prepare gels with selective absorption properties. The second route is based on the reaction between CE and a monofunctional molecule containing a reactive double bond (4-pentenoyl chloride): the product is crosslinked by UV radiation. In this case the crosslinking degree increases with the time of exposure, without variation in chemical composition. Therefore, it was possible to obtain an increase in stability of the liquid crystalline order with the degree of crosslinking.

In this paper we give the results concerning new gels of CE, crosslinked according to the second route. Methacryloyl chloride (MACl) is used as unsaturated compound. Besides the liquid crystalline order, the swelling in DMAc/5%LiCl and water is studied.

## EXPERIMENTAL

### Materials

A sample of CE having $DP_v = 250$ was obtained from Lenzing Viscosa. *N,N*-DMAc (Fluka Chemica) was used after distillation under reduced pressure and stored over molecular sieves. MACl (Fluka Chemica) was used as received.

### Methods

CE methacrylate (CEMA) was obtained by adding a suitable amount of MACl diluted in DMAc to a mother solution of CE in DMAc/5% LiCl at a polymer concentration $C_p = 2\%$ (w/w). The molar ratio between of MACl to glucosidic units was in the range 3–11. The weight of CE used in each synthesis was about 1 g. Two sets of experiments were performed at $T = 5°C$ and 50°C, allowing the reaction to proceed for 2.5 h. The samples, after precipitation by diethyl ether and washing with hot water, were dried in vacuum oven at 50°C for 24 h. The degree of substitution (DS), defined as the average number of oxydryls reacted with MACl per glucosidic unit, was determined by the ponderal method described in Ref.[3]. Its value was between 0.1 and 1.3. A sample having a DS > 0.3

may be easily dissolved in DMAc/5%LiCl by stirring at room temperature. Thermal activation ($T \sim 80^\circ C$) was necessary to dissolve samples of a lower DS.

The crosslinking reaction was performed on solutions of CEMA at $C_p = 4\%$ poured into a quartz mould and irradiated with a 6000 W xenon lamp. Irradiation time $t$ was between 10 and 240 min.

The swelling ratio (SW) of the gel, defined as $SW = W/W_0$ (where $W_0$ and $W$ are the weights of the dry and swollen gel respectively), was determined by the ponderal method, after equilibration with the solvent for about 1 month.

The liquid crystal behaviour was observed by using a Reichert Polyvar Pol optical microscope in polarized light.

The viscosities of the CEMA samples were determined by using a suspended-level Ubbelohde viscometer having a flow time for the solvent higher than 100 s, at $25 \pm 0.1^\circ C$. Solution concentrations varied between 0.4 and 0.2 g/100 ml.

The polymer densities $\rho$ were determined by using a gradient column based on $n$-heptane and carbon tetrachloride, at $25^\circ C$. Density values are reported in *Table 3* and used to determine the chain diameter $d$ according to the relation[10]

$$d = (M_0/\rho N_a L_0)^{1/2}$$

where $M_0$ is the repetition unit molecular weight, $L_0$ is the projection of the repetition unit on the chain axis ($L_0 = 5.14$ Å) and $N_a$ is Avogadro's number. Raman spectra of CEMA samples were recorded by using a Bruker RFS-100 spectrometer.

## RESULTS AND DISCUSSION

The reaction between the oxydril groups of the CE and MACl allows the introduction of unsaturated lateral groups along the polymer chain.

The double bonds may be used for crosslink processes, as well as for other kinds of reaction (i.e. grafting processes). As reported in the Experimental section, the DS varies from 0.1 to 1.3, depending on two main parameters: the molar ratio between MACl and the glucosidic unit ($CE_u$) and the temperature. *Table 1* gives the synthesis conditions and the final DS at 5 and $50^\circ C$. Raman spectra of samples CEMA1, CEMA5 and CEMA9 are shown, as an example, in *Figure 1*. The absorption at 1715 cm$^{-1}$ and 1637 cm$^{-1}$ corresponds to the carbonyl and double bond respectively and demonstrates the presence of methacryloyl residues along the cellulosic chains. Moreover, the amount of double bonds increases, as expected, with the ratio $MACl/CE_u$.

The trend of DS *versus* $MACl/CE_u$ ratio is illustrated in *Figure 2*. The remarkable influence of temperature ($MACl/CE_u$ value being equal) allows the choice of conditions to obtain specific DS values. As we will see in

**Table 1** Synthesis conditions of CEMA

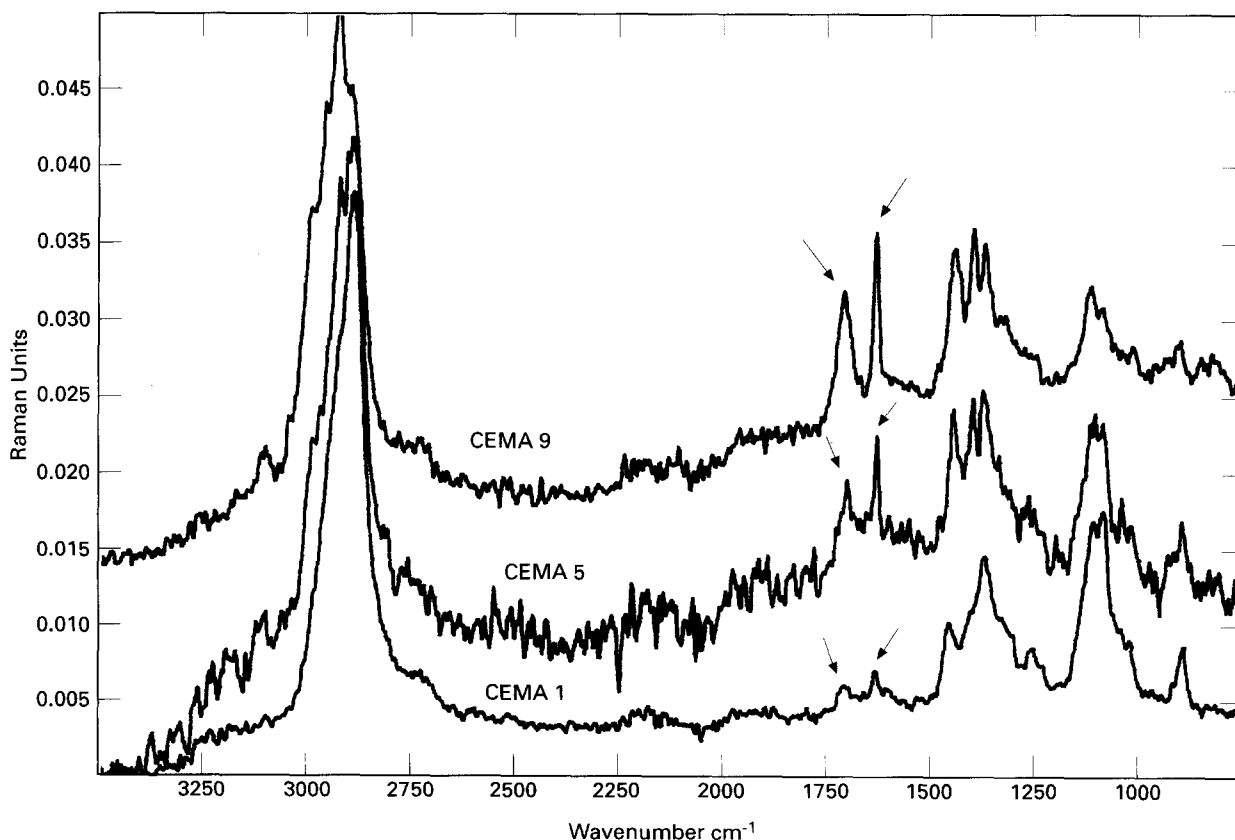| Sample | MACl/CE$_u$ (mol/mol) | $T$ (°C) | DS |
|--------|------------------------|----------|------|
| CEMA1  | 3.66 | 5  | 0.13 |
| CEMA2  | 5.88 | 5  | 0.27 |
| CEMA3  | 8.67 | 5  | 0.35 |
| CEMA4  | 9.00 | 5  | 0.38 |
| CEMA5  | 9.69 | 5  | 0.42 |
| CEMA6  | 10.92 | 5 | 0.43 |
| CEMA7  | 3.03 | 50 | 0.43 |
| CEMA8  | 3.00 | 50 | 0.48 |
| CEMA9  | 3.60 | 50 | 0.67 |
| CEMA10 | 5.04 | 50 | 0.87 |
| CEMA11 | 5.19 | 50 | 0.88 |
| CEMA12 | 6.00 | 50 | 1.02 |
| CEMA13 | 10.86 | 50 | 1.34 |



**Figure 1** Raman spectra of CEMA samples. The arrows indicate the absorption of carbonyl group and double bonds
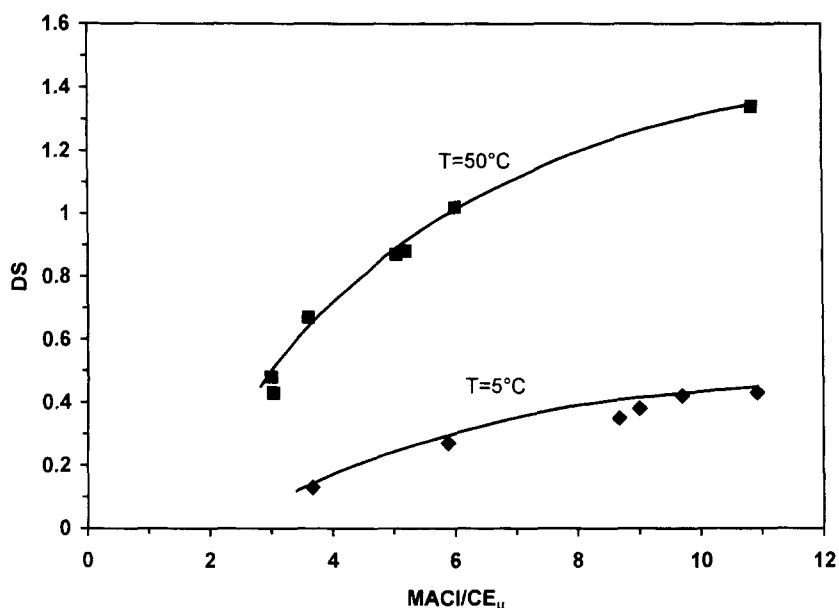
**Figure 2** Trend of DS *versus* $MACl/CE_u$ ratio at 50°C (■) and 5°C (♦)

**Table 2** Molecular parameters of CEMA samples

| Sample | $M_o$ g/mol | $M_1$ | $M$ | $[\eta]^a$ (dl g$^{-1}$) | $\delta$ (g ml$^{-1}$) | $d$ (Å) | $q$ (Å) |
|--------|------------|-------|-------|--------------------------|------------------------|---------|---------|
| CE | 162 | 31.5 | 40 500 | 2.90 | 1.520 | 5.87 | 120 |
| CEMA2 | 180 | 35.0 | 45 000 | 1.82 | 1.470 | 6.30 | 82 |
| CEMA4 | 188 | 36.5 | 47 000 | 1.65 | 1.469 | 6.43 | 72 |
| CEMA6 | 191 | 37.2 | 47 750 | 1.55 | 1.463 | 6.50 | 68 |
| CEMA9 | 208 | 40.4 | 52 000 | 1.26 | 1.440 | 6.83 | 57 |
| CEMA11 | 221 | 43.2 | 55 250 | 0.92 | 1.410 | 7.13 | 43 |
| CEMA12 | 231 | 45.0 | 57 750 | 0.80 | 1.397 | 7.31 | 40 |

$^a$ In DMAc/5% LiCl at 25°C

the following, a DS suitable for our purposes should be neither too small (difficulties in dissolving CEMA and weak gels) nor too high (increased chain flexibility, difficulty in developing liquid crystalline order). With respect to the last point, we must remember that the intramolecular hydrogen bonds, which are one of the main factors responsible for the chain rigidity of CE, are completely destroyed when DS → 3. In a recent study on CE propionate[11] we found that an increase of DS from 0 to ≈ 1 causes a decrease of the main chain rigidity, as expressed by the persistence length $q$ changing from 120 Å (for pure CE) to about 70 Å (for CE mono-propionate). Obviously, this result cannot be extended from a quantitative point of view to any CE derivative one might choose, as, besides the DS, the influence of the chemical nature of the lateral groups on the polymer–solvent interaction cannot be disregarded.

*Table 2* collects the macromolecular characteristics of six CEMA samples, their intrinsic viscosity in DMAc/5% LiCl and the values of the persistence length $q$ according to Yamakawa–Fujii theory[12].

Yamakawa and Fujii[12] developed an equation giving the $[\eta]/M$ dependence for worm-like chains:

$$[\eta] = \phi L'^{3/2}/\lambda^3 M \tag{1}$$

where $L' = \lambda M/M_1$ is the reduced contour length, $\lambda = 1/2q$ and $\phi$ is a function of the reduced diameter $d' = \lambda d$ and $L'$, tabulated by Yamakawa and Fujii. $M_1$ is the mass for unit length, $M_1 = M_o/L_o$.

From equation (1) it is possible to calculate $[\eta]$ as a function of $q$, at a given $M$, $M_o$ and $d$. The values of $q$ which satisfy the condition $[\eta]_{calculated} = [\eta]_{experimental}$ are taken as $q$ for the sample.

*Figure 3* gives the trend of $q$ *versus* DS for CEMA and CE propionate (dotted line). The decrease of $q$ with DS is a common characteristic for both the systems, but the methacrylic lateral groups cause a decrease of $q$ that is stronger than that observed for propylic groups. One consequence of this result is that the critical polymer concentration $C'_p$ for the transition from the isotropic to liquid crystalline phase should be higher for CEMA than for CE propionate. Values of $C'_p$ are reported in column 5 of *Table 3*.

For this system, when the DS increases from 0 to 0.5, the $C'_p$ becomes more than doubles. The molecular parameters, persistence length $q$, chain diameter $d$, axial ratio of the Kuhn segment ($X = 2q/d$) are also listed in the same table. From these values the characteristic volume fractions $V'_p$ at which the anisotropic phase should form on the basis of Flory's theory may be calculated[10]. The results are reported in the last column ($V'_{p\ th}$). These values were compared with the experimental ones ($V'_{p,exp}$) upon conversion of $C'_p$ to $V'_p{}^{12}$. For all the samples $V'_{exp} < V'_{th}$.

In a previous paper[13] we discussed the origin of the difference between theoretical and experimental $V'_p$ for the CE in terms of the existence of anisotropic interactions which, according to Flory' theory, stabilize the anisotropic
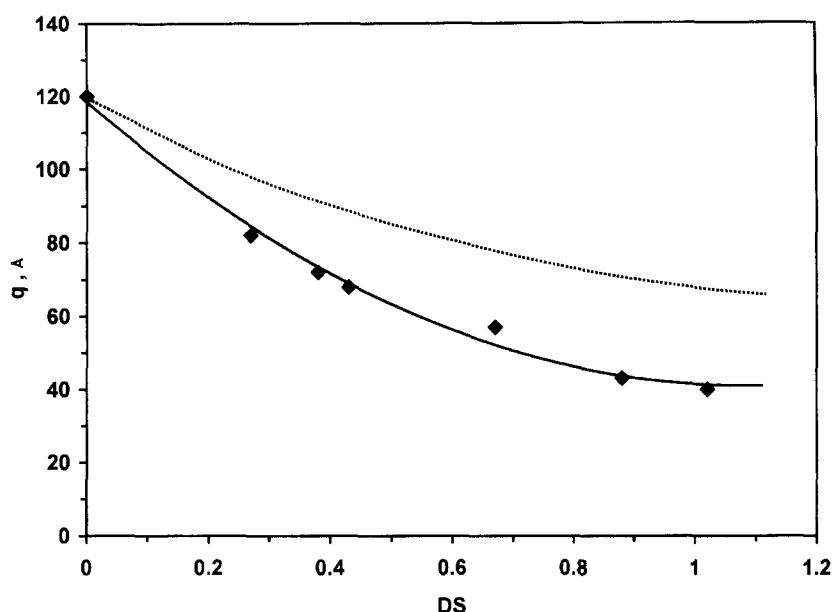
**Figure 3** Persistence length $q$ versus DS for CEMA samples (full line) and CE propionate (dotted line)

**Table 3** Liquid crystalline behaviour of CEMA samples

| Sample | $q$ | $d$ | $X$ | $C_p^{'}$ | $V_{p\ exp}^{'}$ | $V_{p\ th}^{'}$ |
|--------|-----|-----|-----|-----------|------------------|-----------------|
| CE     | 120 | 5.87 | 40.9 | 12.0 | 0.08 | 0.19 |
| CEMA4  | 72  | 6.50 | 22.1 | 19.5 | 0.14 | 0.34 |
| CEMA6  | 68  | 6.50 | 20.9 | 24.5 | 0.18 | 0.36 |
| CEMA9  | 50  | 6.83 | 14.6 | 32.0 | 0.24 | 0.50 |
| CEMA12 | 40  | 7.31 | 10.9 | 45.0 | 0.36 | 0.65 |

phase[14,15]. From this point of view, the progressive introduction of the methacryloyl lateral group does not seems to have big effects compared with pure CE.

All the results suggest that a crosslinking process of CEMA should give gels which are swellable in polar solvents and which show optical anisotropy.

This study was performed by using sample 5 (DS = 0.42) for all experiments. That sample was selected as suitable to prepare gels having a different crosslinking degree and, at the same time, to maintain a good rigidity of the chains connecting the crosslinking points. Three solutions in DMAc/5% LiCl, having $C_p = 1.45\%$, 2.96% and 10% (w/w) were irradiated for a period of time in the range 10–240 min. *Table 4* collects the crosslinking conditions and SW values in DMAC/5% LiCl at 25°C, obtained after a long period for each sample in a large amount of solvent ($\approx$ 3 weeks). The decreasing trend of SW versus irradiation time is highlighted in *Figure 4*.

The SW ratio is quite high when irradiation time is of the order of a few minutes or tens of minutes and rapidly decreases towards a plateau when the time is about 100–200 min, indicating the approach to a maximum crosslinking degree. Moreover, SW is lower the higher is the polymer concentration of the initial solution: at a given irradiation time SW halves when $C_p$ varies from 1.5 to 3% and then reduces further, but to a lesser extent, when $C_p = 10\%$. The lack of linearity of SW versus $C_p$, at constant $t$, probably depends on the increased overlapping of the semirigid chains. At $C_p = 10\%$ the system is not far from the condition at which the anisotropic phase becomes stable and pretransitional effects may set up and influence both the solution and the gel states.

**Table 4** Swelling of CEMA gels in DMAc

| $t$ (min) | SW (w/w) | | |
|-----------|----------|---|---|
| | $C_p = 1.50\%$ (w/w) | $C_p = 3\%$, (w/w) | $C_p = 10\%$ (w/w) |
| 10  | —   | 122 | —  |
| 15  | 163 | 82  | 60 |
| 30  | 114 | 52  | 40 |
| 45  | 83  | 49  | —  |
| 60  | —   | 41  | —  |
| 90  | 75  | 38  | 20 |
| 240 | 66  | 31  | 16 |

Some of the samples listed in column 3 of *Table 4* were progressively swelled in DMAc/5% LiCl at 25°C and observed under polarized light. At low SW ratio all the gels show optical anisotropy. A further increase of SW causes a transition to an isotropic gel. The corresponding value of polymer concentration $C_p^{'}$ is characteristic of each sample.

*Figure 5* shows the trend of $C_p^{'}$ with 1/SW; the value at 1/SW = 0 corresponds to $C_p^{'}$ of the uncrosslinked polymer. Therefore, the critical concentration for the transition from isotropic to anisotropic gel, and vice versa, decreases as 1/SW increases. This trend confirms the results previously obtained for chemical crosslinking of pentenoyl CE[3] and for some physical gels of CE[16,17] and chitin[18]. These latter gels were obtained by humidification of layers of diluted polymer solutions in DMAc/LiCl; water absorption causes the formation of gellified films which progressively shrink. When the polymer concentration inside the film reaches a characteristic concentration $C_p^{'}$, cholesteric textures are observed. The $C_p^{'}$ values are always lower than the $C_p^{'}$ in
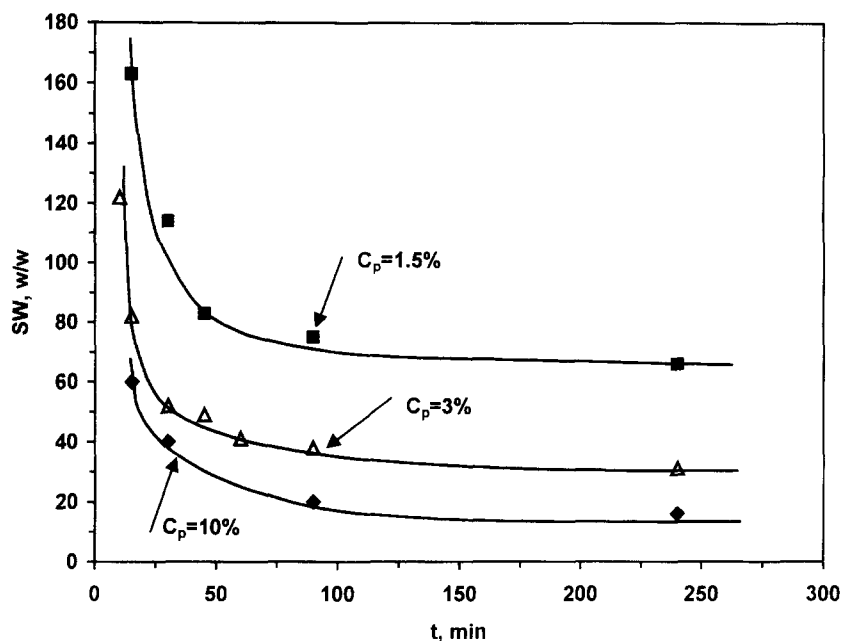
**Figure 4**  SW *versus* irradiation time *t* for CEMA5. Different lines correspond to different concentration of the initial solution
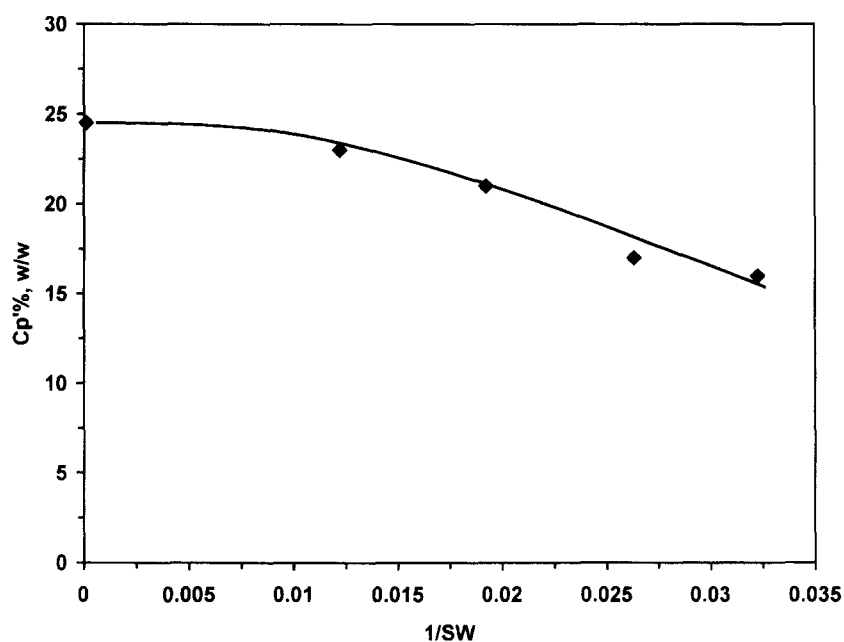


**Figure 5**  Critical concentration for the appeararance of the LC phase plotted *versus* the inverse of SW

molecular solutions. Even though it may be questionable to compare the transition observed in solution with that observed in the gel state, it should be remembered that stabilization of the ordered phase inside a network based on freely joined rods or worm-like chains is predicted by different theories and observed for thermotropic polymers[4,19–21].

One final result concerns the swelling behaviour of our samples in water. Given that we were unsuccessful in direct swelling of dried networks by water, it was possible to replace the DMAc/5% LiCl by immersion of gels in pure water. A progressive shrinking up to equilibrium conditions was observed. Periods of time as long as 1 month are necessary to reach a constant SW. *Figure 6* shows the trend of SW *versus t*; the SW ratios vary between $\approx$ 30 and $\approx$ 15, depending on the irradiation time: these values are about a

half of those observed in DMAc/5% LiCl. Attempts to improve the hydrophilic behaviour by solfatation of CEMA are in progress.

CONCLUSION

Synthesis of CEMA has been performed in homogeneous conditions by reaction of CE dissolved in DMAc/5% LiCl with MACl. By controlling the temperature, the polymer concentration and the molar ratio of the reagents one can obtain derivatives with a specific DS.

CEMAs posses peculiar properties: first of all they are soluble to a large extent in the same solvent used for the derivatization process. Secondly, concentrated solutions show lyotropic properties. The critical concentration at which the anisotropic phase becomes stable increases with
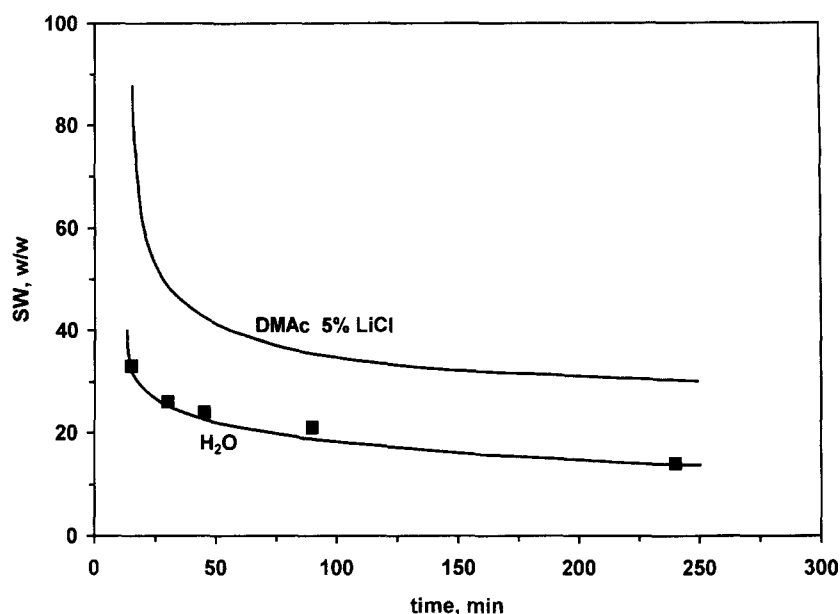
**Figure 6** SW in $H_2O$ and DMAc/5% LiCl for CEMA5 at different irradiation times

DS, as observed for other derivatives[11,24]. Finally, the presence of double bonds along the chain makes the derivative a reactive product, which may be used for different purposes: grafting of polymer chains[22,23], preparation of networks from crosslinking reactions, etc.

In this paper we have discussed how to obtain gels by simple UV irradiation: it was shown that the amount of solvent (DMAc/5% LiCl) which swells 1 g of product in equilibrium condition decreases as the irradiation time increases. SW values as high as 160–120 (w/w) were obtained at low irradiation time by crosslinking solutions containing from 1.5 to 3% of CEMA. All of the gels show optical anisotropy when swelled below critical $C'_p$ values; this process is reversible and it is related to the iso $\leftrightarrow$ aniso transition of the unswelled polymer. Finally, the solvent DMAc/LiCl may be replaced by water after keeping the gels in pure water for a long period. SW values are lower with respect to DMAc/LiCl, but may be considered as a starting point for the preparation of hydrogels based on CE.

## REFERENCES

1. Yang, Y., Kloczkowski, A., Mark, J. E., Erman, B. and Bahar, I., *Macromolecules*, 1995, **28**, 4920.
2. Yang, Y., Kloczkowski, A., Mark, J. E., Erman, B. and Bahar, I., *Macromolecules*, 1995, **28**, 4927.
3. Marsano, E., Bianchi, E., Boero, E., Gastaldi, G. and Focher, B., *Polym. Adv. Technol.*, 1995, **6**, 727.
4. Aharoni, S. M., *Synthesis, Characterization and Theory of Polymeric Networks and Gels.* Plenum Press, New York, 1992.
5. Kishi, R., Sisido, M. and Tazuke, S., *Macromolecules*, 1990, **23**, 2779.
6. Kishi, R., Sisido, M. and Tazuke, S., *Macromolecules*, 1990, **23**, 3868.
7. Sisido, M. and Kishi, R., *Macromolecules*, 1991, **24**, 4110.
8. Suto, S. and Tashiro, H., *Polymer*, 1989, **30**, 2063.
9. Mitchell, G. R., Guo, W. and Davis, F. J., *Polymer*, 1992, **33**, 69.
10. Flory, P. J., *Adv. Polym. Sci.*, 1984, **59**, 1.
11. Bianchi, E., Marsano, E., Ricco, L. and Conio, G., *Carbohydrate Polymer*, 1997, **31**, 000.
12. Yamakawa, H. and Fujii, M. M., *Macromolecules*, 1974, **7**, 128.
13. Ciferri, A. and Marsano, E., *Gazzetta Chimica Italiana*, 1987, **117**, 567.
14. Flory, P. J. and Ronca, G., *Mol. Cryst. Liq. Cryst.*, 1979, **54**, 289.
15. Flory, P. J. and Ronca, G., *Mol. Cryst. Liq. Cryst.*, 1979, **54**, 311.
16. Ritchey, A. M. and Gray, D. G., *Biopolymers*, 1988, **27**, 1363.
17. Giasson, J., Revol, J. F., Ritcey, A. M. and Gray, D. G., *Biopolymers*, 1988, **27**, 1999.
18. Bianchi, E., Ciferri, A., Conio, G. and Marsano, E., *Mol. Cryst. Liq. Cryst. Lett.*, 1990, **7**(4), 111.
19. De Gennes, P. G., *Acad. Sci. Ser. B.*, 1986, **101**, 281.
20. Warner, M. and Wang, X. J., *Macromolecules*, 1991, **24**, 4932.
21. Abramchuk, S. S., and Khoklov, *Dokl. Phys. Chem.* 1988, **297**, 1069.
22. Bianchi, E., Ciferri, A., Conio, G., Lanzavecchia, L. and Terbojevich, M., *Macromolecules*, 1986, **19**, 646.
23. Ricco, L., Bianchi, E. and Marsano, E., Grafting of acrylonitrile onto cellulose in homogeneous phase. In *2nd IUPAC-Sponsored International Symposium on Free Radical Polymerization: Kinetics and Mechanisms*, ed. S. Margherita, May 26–31, 1996.
24. Conio, G., Bianchi, E., Ciferri, A., Tealdi, A. and Aden, M. A., *Macromolecules*, 1983, **16**, 1264.