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Metathesis polymerization as a route to water soluble polymers and hydrogels

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Abstract

A ring-opening metathesis polymerization-based method for the preparation of water soluble conjugated polyenes, hydrophobically modified water soluble polymers and polyelectrolyte hydrogels is described. The novelty of the method lies in its ability to produce polymers which contain olefinic unsaturation in the main chain, a structural feature not present in the numerous other examples of naturally occurring and synthetic water soluble polymers. The polymers are described in terms of their solution properties and NMR spectra.

Keywords: Conjugated polymer; Hydrogel; Hydrophobic modification; Metathesis; Polyelectrolyte; Water soluble polymer

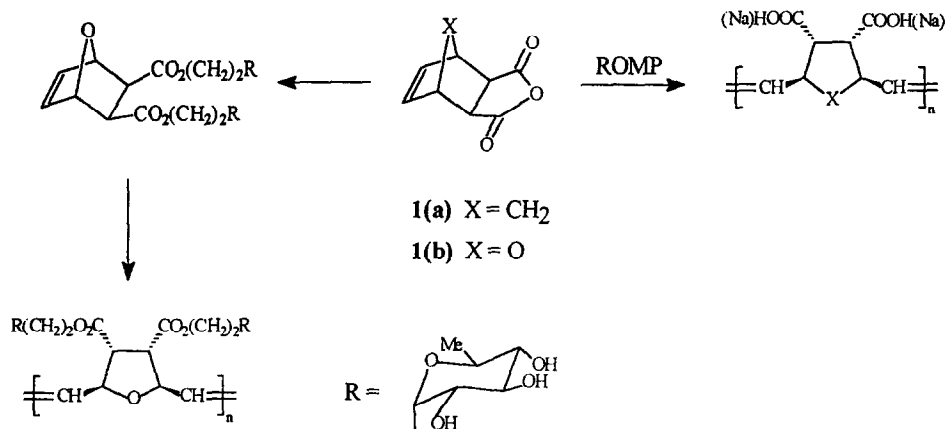
1. Introduction

Water soluble and hydrophilic polymers constitute a structurally diverse and ubiquitous class of materials which are of fundamental importance in biology and of immense commercial utility. A large number of the materials currently in use are either naturally occurring or are derived from biological sources but many are totally synthetic and are prepared by the polymerization of α -olefins by various mechanisms [1]. The few examples that have been prepared by Ring-Opening Metathesis Polymerization (ROMP), Scheme 1, use the readily available *exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride, **1a**, its oxygen bridged

analogue, **1b**, and their derivatives as monomers [2–4], water solubility depending on either carboxylate functionality or the presence of carbohydrate groups [5]. The novelty of the metathesis polymers lies in the fact that they are the only examples of water soluble polymers with olefinic unsaturation in the main chain. The stereochemistry of the main chain may then be varied from high *cis* through to high *trans* using the range of ROMP catalysts, both metal alkylidene and metal salt types which are now available [6,7]. One has then the opportunity to study the changes in solution properties which are related to the different conformations resulting from different proportions of *cis* and *trans* double bonds.

We have recently used ROMP to prepare three different types of water soluble polyelectrolyte including conjugated [8], hydrophobi-

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Scheme 1.

cally modified [9] and hydrogel types [10], with a view to investigating the potential of ROMP in this area.

2. Experimental

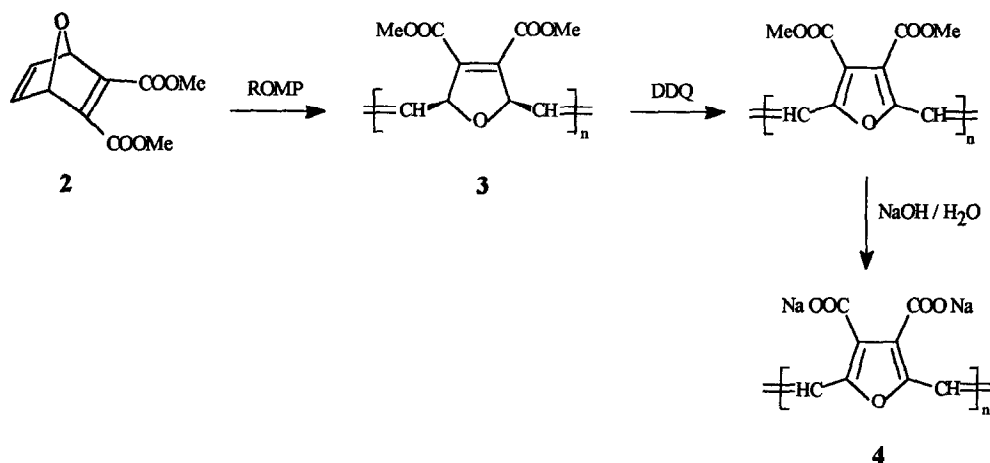
Synthetic and analytical procedures are described in recent publications [8–10]. The variation of % Equilibrium Water Content (%EWC) with pH in cross-linked polyelectrolyte hydrogels was determined in 0.01 M citrate buffer at 25°C. Constant ionic strength was maintained throughout the pH range (2.2–8.0) by the addition of KCl [11]. Hydrogel samples, in the form of discs, were removed periodically from the

buffer solution and weighed, after removal of excess buffer solution with tissue paper, the process being repeated until the hydrogel discs attained a constant weight, Wt_{wet} . At this point the pH of the solution was recorded and the discs were dried in vacuum to constant weight, Wt_{dry} . %EWC is then determined according to the equation:

$$\% \text{EWC} = \left[\text{Wt}_{\text{wet}} - \text{Wt}_{\text{dry}} \right] / \text{Wt}_{\text{wet}} \cdot 100$$

3. Water soluble conjugated polyenes

In some of our earlier experiments the dependence of conformation in solution on the *cis* /



Scheme 2.

trans double bond ratio was demonstrated by the colour change observed in certain water soluble conjugated polyenes which had a different ratio of *cis* and *trans* double bonds [8]. The polymers were prepared by ROMP of 7-oxa-2,3-bismethoxycarbonylbicyclo[2.2.1]hepta-2,5-diene, **2**, using the RuCl_3 catalyst to prepare the high *trans* and the OsCl_3 catalyst to prepare the high *cis* precursors, **3**, which were then dehydrogenated and saponified to yield the water soluble conjugated polyenes, **4**, Scheme 2. In aqueous solution the high *trans* form of **4** is deep purple in colour and the high *cis* form is red–purple, the high *trans* form is also obtained by standing solutions of the high *cis* form in sunlight. The difference in colour reflects the increased conjugation length possible in the more planar conformation that results from the occurrence of long sequences of *trans* double bonds. The different conformational properties of these polymers was further demonstrated when their UV/vis spectra were examined as a function of pH, Fig. 1. In very dilute aqueous solution, in the basic regime ($\text{pH} > 9.5$), when both polymers exist as their Na salts, their absorption maxima differ by only approx. 2 nm. This apparent contradiction may be understood

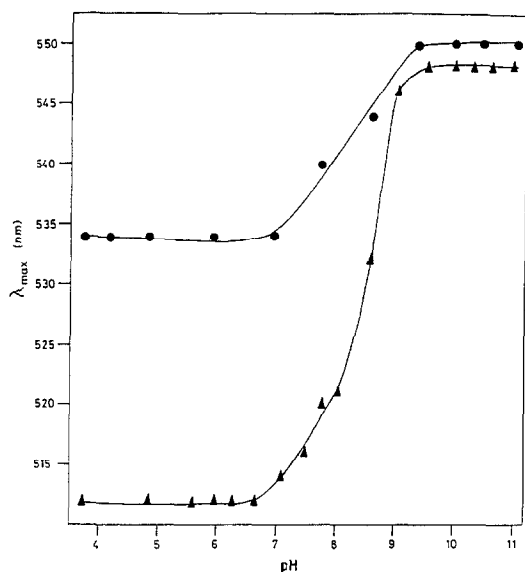


Fig. 1. Plot of λ_{max} vs. pH for aqueous solutions of: 93% *trans* **4**, (●) and 56% *trans* **4**, (▲).

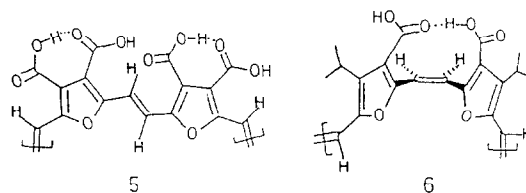


Fig. 2. Intra-ring, **5**, and inter-ring, **6**, modes of hydrogen bonding which may operate at *trans* and *cis* junctions respectively in water soluble conjugated polyenes, **4**.

in terms of both polymers being in an extended and quite planar conformation due to polyanion expansion, a phenomenon well established in dilute solutions of polyelectrolytes [12]. However as the pH is lowered on the addition of dilute acid, the high *cis* form becomes red whilst the high *trans* form remains purple. This difference is reflected in a 36 nm hypsochromic shift in the absorption maximum of the high *cis* form, compared to a shift of only 16 nm in the high *trans* form upon changing from the acidic to the basic regime, Fig. 1.

The different behaviour is attributed to the different modes of hydrogen bonding in the acid form of the polymers which can occur between adjacent furanyl rings depending on the stereochemistry of the linking vinylene moiety, Fig. 2. In high *trans* sequences, **5**, intra-unit hydrogen bonding allows the chain to retain a planar conformation and a relatively high adsorption maximum. However furanyl rings joined by *cis* vinylene units, **6**, can engage in inter-unit hydrogen bonding which greatly diminishes the π -overlap due to the parallel orientation of the furanyl rings. Thus the difference in hypsochromic shift between the high *trans* and high *cis* polymers serves to demonstrate the sensitivity of the conformation of these polymers, in aqueous solution, to changes in the main chain double bond stereochemistry.

4. Hydrophobically modified water soluble polymers

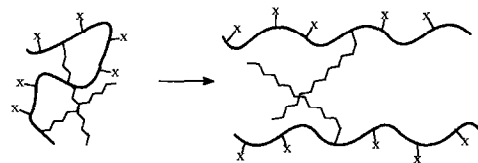
The polymer literature contains numerous examples of novel and useful polymers which

have been formed by chemical modification of common synthetic or naturally occurring precursors. Many other examples exist where copolymerization has led to beneficial modifications. These procedures have been applied with particular success in the field of water soluble polymers where modification with small proportions of hydrophobic groups has produced a whole range of materials which are of great scientific and commercial interest [13].

The *modus operandi* of these materials is derived from a hydrophobic or soap-like interaction which occurs in aqueous solution involving the hydrophobic groups appended to the main, hydrophilic, chain Fig. 3. This leads to the formation of solutions with intrinsic viscosities which may be lower than those of the unmodified form of the polymer (intramolecular association), or orders of magnitude higher (intermolecular association), depending on their concentration relative to a critical concentration, C^* , which is related to various compositional and microstructural features in the polymer. They are therefore widely used in the modification of the rheology of aqueous fluids in the oil, pharmaceutical and paint industries [14]. We have recently described a ROMP route to some novel hydrophobically modified water soluble polymers again using the anhydride monomers **1a** and **1b** as the basic starting materials, Scheme 3.

Two synthetic approaches were adopted. The anhydride monomer, **1a**, may be polymerized in the conventional way using the OsCl_3 catalyst in chlorobenzene, and the polymer then hydrolysed to the acid form, **7a**. Hydrophobic modification is then introduced by a recently described procedure [15] using dodecylamine which leads to a polymer, **8a**, with a random distribution of hydrophobe. Both **7a** and **7b** may be formed conveniently in aqueous media from **1a** and **1b** using K_2RuCl_5 [4], although it should be noted that **1a** will only polymerize using residual catalyst solution from the polymerization of **1b**.

In the second approach the anhydrides are first converted to their dimethyl esters, **9a** and



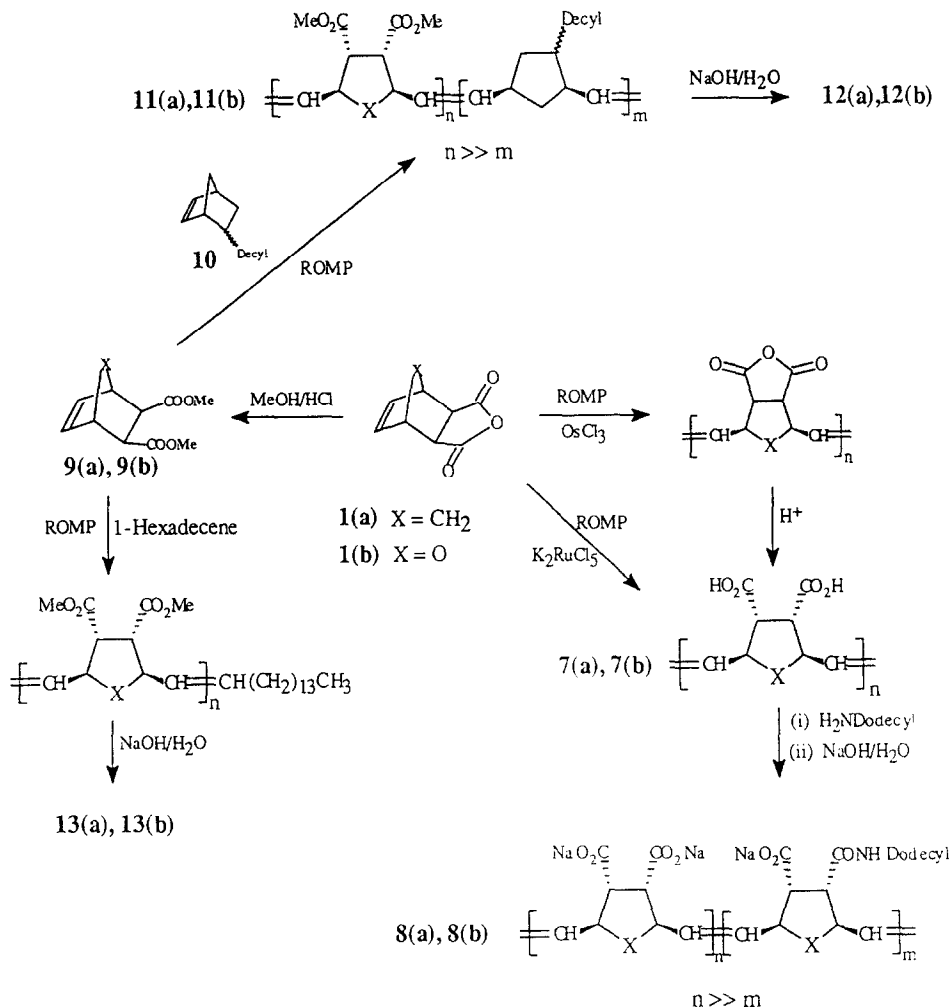
A Dilute Solution ($< C^*$) **B** Semi-Dilute Solution ($> C^*$)

Fig. 3. Hydrophobic interactions in hydrophobically modified water soluble polymers. **A**, Intramolecular, leading to lower viscosities and, **B**, intermolecular, leading to increased viscosity, relative to the unmodified analog.

9b, prior to copolymerization with a hydrophobic comonomer, in this case endo-5-decyl-norbornene, **10**. Use of the dimethyl esters means that the frequently encountered problem of comonomer incompatibility is circumvented; the water soluble sodium salts, **12a** and **12b**, are then produced on base hydrolysis. This method has the advantage of producing polymer in which the hydrophobic moiety is attached by a hydrolytically stable linkage, and it also allows for the possibility of preparing polymers with a blocky distribution of hydrophobe if the living Schrock-type initiators are used [7]. We have also prepared a series of lower-molecular-weight water-soluble polymers, **13a** and **13b**, obtained from **9a** and **9b** by chain transfer to 1-hexadecene and we are currently investigating the potential of these materials to form polymeric micelles in aqueous solution.

With this series of polymers NMR spectroscopy has proved very useful in the determination of several microstructural features which are relevant to the polymers' macroscopic properties. For example, the *cis/trans* ratio of the vinyl units and an estimation of the level of hydrophobe incorporation, may be obtained from the ^1H NMR spectra of the polymers. Copolymer composition can be obtained by comparing the integrals of the side chain resonances with those of the well resolved $\text{H}^{5,6}$ protons, Fig. 4. These features may also be determined from the spectra of the methyl esters prior to hydrolysis, where the spectral resolution is in fact better.

The distribution of the hydrophobic units



Scheme 3.

along the polymer chain is important, and within a given system a change in this parameter can lead to the predominance of either inter- or intramolecular association and widely different solution properties [16,17]. Hence ¹³C NMR is particularly useful because of the dependence of the chemical shift of various carbon atoms on their placement in either homo (M₁M₁) or hetero (M₁M₂) compositional dyads. An example of this is seen in Fig. 5 which is the C^{1,4} region of the spectrum of the dimethyl ester copolymer, **11b**. C⁴ in the homo dyad is a multiplet centered at 80.5 ppm, whereas in the hetero dyad units this resonance is downfield at 82.2 ppm. Comparison of the integrals of these sig-

nals, combined with an estimate of the hydrophobe content, from either ¹H or ¹³C spectra, shows that the hydrophobe is distributed in a random manner, within the limits of the inherent inaccuracies in such measurements.

Dilute solution viscometry of each of the water soluble polymers shows the expected non-linear relationship between η_{sp}/c and c resulting from polyanion expansion, *vide supra*. Linear plots, however, are obtained by plotting $(\eta_{sp}/c)^{-1} \nu \sqrt{c}$ or, alternatively, carrying out the measurements in 0.1 mol dm⁻³ NaBr solution with isotonic dilution, this behaviour is typical of polyelectrolytes in aqueous solution [12].

Of greater significance is the observation that

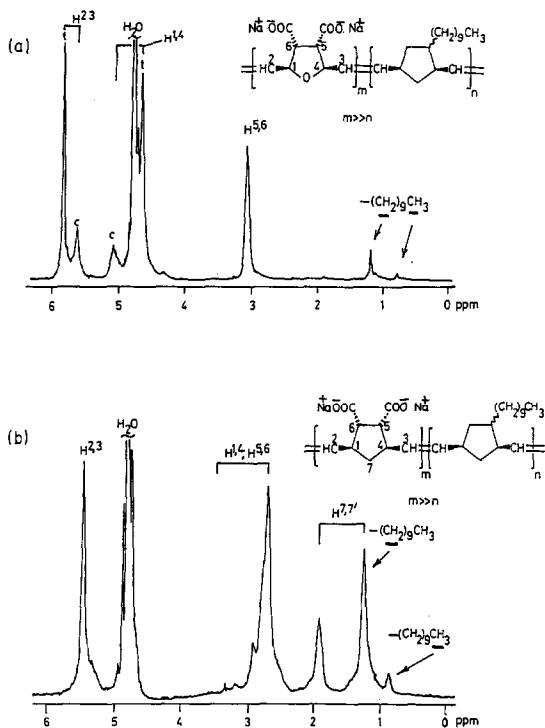


Fig. 4. Representative ^1H NMR spectra of hydrophobically modified water soluble polymers prepared by the copolymerization technique; (a), furanyl series, 19% *cis*; (b), cyclopentyl series, 8% *cis*.

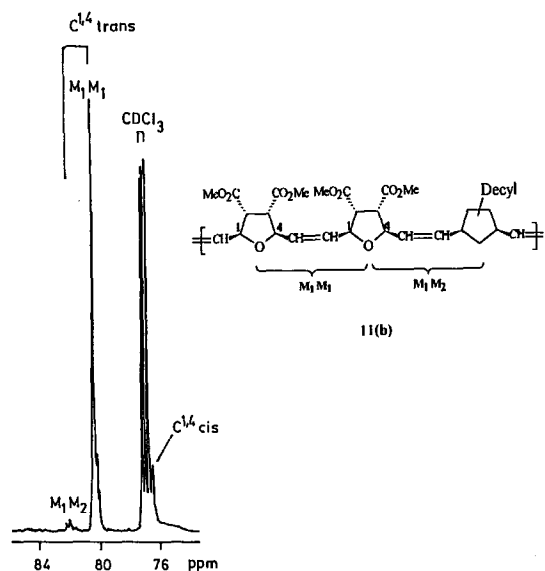


Fig. 5. Determination of the distribution of hydrophobic group using 125 MHz ^{13}C NMR. $\text{C}^{1,4}$ region of the spectrum of furanyl polymer **11b** showing resonances from homo and hetero dyad units.

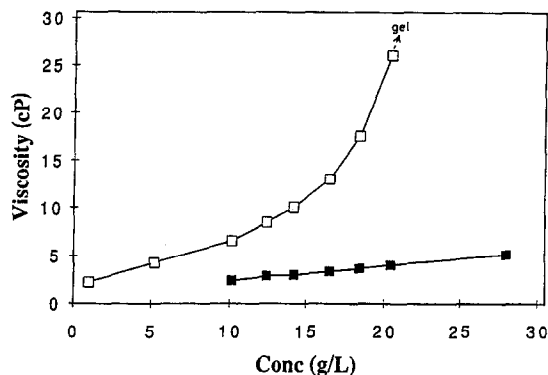


Fig. 6. Concentration dependence of Brookfield viscosity of aqueous solutions of polymer **12a**, (\square) and its unmodified analogue **7a**, (\blacksquare).

at a concentration of 20 g dm^{-3} the Brookfield viscosity of the copolymer **12a** is five times higher than of its unmodified analogue. This phenomenon [13] is due to the intermolecular interaction of the hydrophobic side chains and the formation of multi-molecular aggregates, Fig. 3. Furthermore, dilution of a solution of the unmodified polymer, i.e. **7a**, results in a linear decrease in viscosity whereas dilution of the hydrophobically modified form, **12a**, shows a strongly nonlinear decrease in viscosity, Fig. 6. This rheological behaviour is characteristic of the hydrophobic effect and is seen in many other examples of hydrophobically modified water soluble polymers [13,14].

5. Polyelectrolyte hydrogels

In contrast to the water soluble polymers described above almost all examples of metathesis polymer are extremely hydrophobic. However, metathesis polymerization may also be used to prepare polymers exhibiting intermediate behaviour; although insoluble they absorb water and swell to various extents, the swollen piece of polymer often containing $> 90\%$ of its weight in water whilst retaining its original shape [10]. Many other hydrogels have been prepared by a variety of polymerization tech-

niques and are widely used in the pharmaceutical industry [18–20].

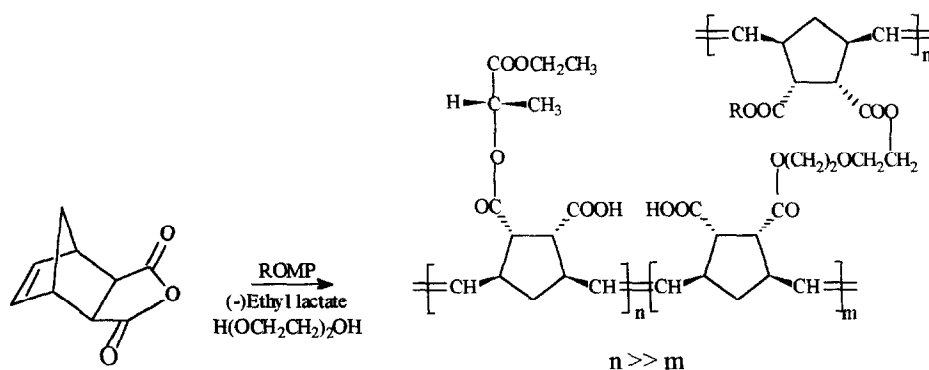
Using a ‘one-pot’ synthetic route, based on the anhydride **1a**, a series of partially esterified polymers was prepared [10]. The anhydride monomer is mixed with an OsCl_3 or RuCl_3 catalyst using the particular alcohol or diol required to provide the ester functionality as the solvent. Diester repeating units result when simple alcohols such as methanol or propanol are used but half-ester is the main product when using more complex and bulkier alcohols such as diethyl tartrate or menthol. In either case the degree of esterification increases as reaction time and reaction temperature are increased, the more severe conditions sometimes resulting in the formation of insoluble crosslinked materials. Shorter reaction times lead to soluble polymers which may be cast from solution into strong transparent films of various thicknesses and in this form the materials are suitable for the determination of the percent equilibrium water content (%EWC).

The uptake of water in these materials is dependent on the polarity of the ester function and we observed, in neutral solution, values for the EWC ranging from 25% to 83% with polar ester functionality. However, the EWC for polymers with less polar groups such as *n*-propyl or methyl fell to 10% or less.

As expected with the half-ester polymers, containing the $-\text{COOH}$ function appended to

the main chain, the %EWC is highly pH dependent. However, quantitative studies at high pH were hampered because the swollen polymer begins to break up, eventually dissolving. Earlier work [10] had shown that polymers prepared in the presence of various diols formed highly crosslinked and insoluble materials over a wide pH range. Therefore the problem of polymer solubility at high pH was resolved by adding small amounts of diol, such as diethylene glycol (DEG), to the one-pot polymerization procedure which rendered the product insoluble without substantially compromising the EWC, Scheme 4.

Fig. 7 shows the variation of %EWC with pH for some of the optically active hydrogels which is analogous to the behaviour of other hydrogel systems although the pH range (~ 2 units) between minimum and maximum %EWC is significantly broader. This represents a continuous transition, as opposed to the discrete transition observed for example for sodium polyacrylate [21,22]. A possible explanation for this contrast may be the greater stiffness of the polymer chain which contains 1,3-pentylene rings. Inspection of Fig. 7 also shows that various synthetic factors may influence the properties of these materials. For example, increasing the concentration of crosslinking diol, and presumably the crosslink density, has the predictable effect of lowering the EWC throughout the pH range. Also, the polymer prepared using the



Scheme 4.

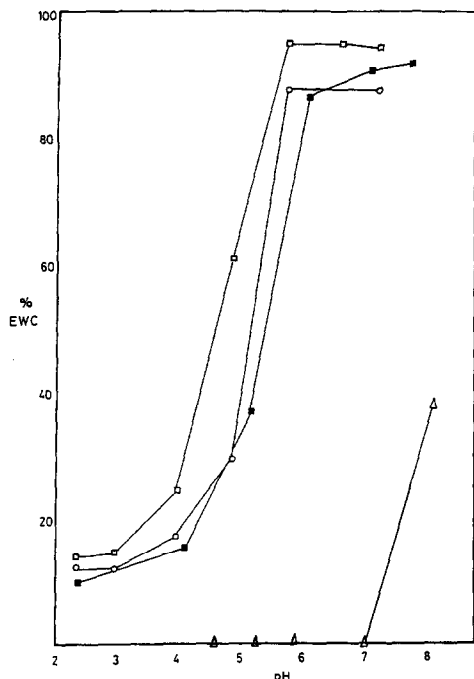


Fig. 7. Variation of %EWC as a function of pH (recorded after the attainment of maximum water uptake) for polyelectrolyte hydrogels prepared from **1a** in the presence of (–) ethyl lactate using the OsCl_3 catalyst and 5 mol% DEG, (\square); 10 mol% DEG, (\circ); using the RuCl_3 catalyst and 5 mole% DEG, (\blacksquare); and in the presence of (–)-menthol in the absence of crosslinking agent, (\triangle).

RuCl_3 catalyst has a lower EWC than that made with OsCl_3 , using the same amount of crosslinking agent. These features are still under investigation and may be due to a number of factors such as the degree of crosslinking/esterification and molecular weight differences. Fig. 2a also shows dramatic differences in behaviour when the highly hydrophobic (non-crosslinked) menthyl ester is used. Under the same conditions as those used for the other polymers this polymer does not start to swell until the pH is greater than 7. These observations mean that it will be possible to tailor the properties of the polymers by changing various structural features such as the hydrophobicity of the ester moiety and the crosslink density.

As with the water soluble polymers described

earlier, the stereochemistry of the main chain double bonds can be varied by using different catalyst systems, which should allow further control of the polymer properties. All of these features are the subject of ongoing studies.

6. Conclusions

It has been demonstrated that ROMP can be used to prepare a number of different types of water soluble and water swellable polymers from readily available monomers. Each of these materials have properties which are consistent with those of analogous polymers prepared by conventional routes. However, this methodology is important in that it permits a wide variation of the polymer microstructure and composition with the resulting opportunity for tailoring of the macroscopic properties of the materials.

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