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# Cellulose Containing Block Copolymers

## 2. Molecular Weights and Solution Properties of Trimethylcellulose – Poly(oxytetramethylene) Block Copolymers

**C. Feger* and H.-J. Cantow**

Institut für Makromolekulare Chemie der Universität Freiburg, Hermann-Staudinger-Haus,
Stefan-Meier-Straße 31, 7800 Freiburg i.Br., Federal Republic of Germany

## SUMMARY

Solution properties of trimethylcellulose-poly(oxytetramethylene two and star block copolymers with defined molecular weights are reported. The solubility behavior of the concerned block copolymers is mainly governed by the solubility of the trimethylcellulose blocks. The solubility parameters for TMC and POTM indicate that both polymers are incompatible with each other. This is confirmed by the appearance of phase separation in concentrated solutions of corresponding blends even in nonselective solvents. Intrinsic viscosities of the block copolymers are reported and compared to corresponding polymer blend solutions.

In a previous paper1) we have described a synthetic route to trimethylcellulose-poly(oxytetramethylene) block copolymers via acidolytic cleavage of high molecular trimethylcellulose (TMC) with waterfree hydrogen chloride and treatment of the resulting chlorine terminated TMC prepolymers with silverhexafluoroantimonate ($AgSbF_6$) in the presence of tetrahydrofuran (THF). Monofunctional termination of the initiated living THF block polymerization leads to TMC-poly(oxytetramethylene) (POTM) two block copolymers. Low molecular weight poly(4-vinylpyridine) as terminating agent yields star shaped block copolymers, where POTM forms the center blocks.

In this paper we describe some molecular weight dependent properties of TMC-POTM block copolymers prepared by the mentioned route. However, due to the complex behavior of the obtained block copolymers fully conclusive interpretations of the observed effects can not be presented.

## MOLECULAR WEIGHT DETERMINATION

As has been shown1) the number average molecular weight of the TMC prepolymers is governed by the kinetics of the acidolytic cleavage according2)

$$\ln(1 - 1/P_o) - (1 - 1/P_t) = kt \qquad (1)$$

with $P_o$ and $P_t$ , respectively, the degree of polymerization of the undegradated TMC and after cleavage time t, respectively.

Because the acidolytic cleavage of the glycosidic bond in cellulosics leads to two types of endgroups, one unreactive TMC

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* Present address: Polymer Science and Engineering Department University of Massachusetts, Amherst, USA

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block - without α-chloroether end group - is formed per original TMC macromolecule. The amount of those unreactive blocks is governed by the degree of polymerization of the initial ($P_o$) and of the cleaved TMC ($P_t$)

$$\% \text{ non reactive TMC} = (P_t/P_o) \cdot 100 \quad . \qquad (2)$$

The initiator concentration available for the THF block copolymerization is equal with that of the α-chloroether terminated TMC blocks obtained by cleavage of one mol TMC macromolecules

$$\text{mol initiator} = (P_o/P_t) - 1 \quad . \qquad (3)$$

The polymerization of THF in the considered system is a living type as was proven[1]. Consequently the number average degree of polymerization is given by[3]

$$P_n = [M]/[I] \quad , \qquad (4)$$

when [M] indicates the concentration of the polymerized monomer and [I] the one of the initiator.

In the considered TMC-POTM block copolymers [M] was determined first by the weight increase of the samples and second by elemental analysis. With the concentration of the initiator known by the degradation kinetics (eq. 3) and considering the amount of unreactive TMC blocks (eq. 2) the number average molecular weightsof the POTM blocks have been evaluated (Tab. I). Of course, these values are valid only concerning impurity free systems. Consequently the actual POTM molecular weights will be somewhat higher in our system.

Table I: TMC-POTM block copolymers; number average molecular weights ($M_n$) of TMC and POTM blocks, TMC homopolymer content and intrinsic viscosities of the TMC prepolymers and of the block copolymers. POTM molecular weights correlated to uncoupled blocks ([η] in l/g)

| Sample | $M_n$ TMC [Dalton] | $M_n$ POTM [Dalton] | Homo TMC cont. [%] | POTM cont. [%] | [η]TMC prepol. | [η]bl. copol. |
|---|---|---|---|---|---|---|
| 1 | 27500 | 6100 | 23.3 | 14 | .147 | .111 |
| 2 | 20600 | 36000 | 7.2 | 59 | .114 | .238 |
| 3 | 17800 | 293500 | 1.0 | 94 | .102 | .790 |
| 4 | 17600 | 65500 | 3.6 | 76 | .101 | .750 |
| 5 | 32000 | 115300 | 14.4 | 67 | .177 | .700 |
| 6 | 70000 | 219000 | 26.1 | 56 | .330 | .415 |
| 7 | 13000 | 11000 | 6.3 | 43 | .775 | .098 |
| 8 star | 13000 | 16500 | 5.1 | 53 | .078 | .131 |
| 9 star | 27000 | 62400 | 8.3 | 64 | .146 | .470 |
| 10 | 27000 | 19700 | 14.6 | 36 | .146 | .165 |
| 11 star | 27000 | 41100 | 10.5 | 54 | .146 | .195 |

## MOLECULAR WEIGHT DISTRIBUTION

As shown[1] the molecular weight distribution of the TMC blocks obtained by random acidolytic cleavage is rather broad (SCHULZ-FLORY type distribution). Because of the living character of the THF polymerization the molecular weight distribution of the

POTM blocks is expected to be more narrow than the one of the TMC blocks. However, due to unavoidable impurities in the TMC-THF solution the actual POTM distribution should have a tendency to be broader than a POISSON type distribution. Thus GPC measurements of TMC-POTM two block copolymers show up a heterogeneity comparable to that of the TMC prepolymers (Fig. 1). The TMC-POTM star block copolymers - Fig. 2 - exhibit a much broader distribution, due to the additional nonuniformity arising by the branch number. It is obvious that the the coupling in such systems is incomplete as evidenced by the UV-analysis ($\lambda$ = 252 nm) of the star center, poly(4-vinylpyridine) ($M_n$ = 3.000). Consequently a remarkable amount of monobranched TMC-POTM block copolymers with poly(4-vinylpyridine) end groups occurs. A certain amount of TMC homopolymer and of TMC-POTM two block copolymers terminated by impurities is present.

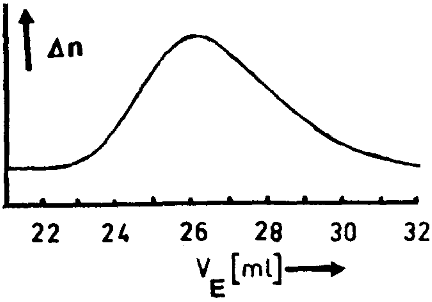

Figure 1: HPLC-GPC elution curve of TMC-POTM two block copolymer 5

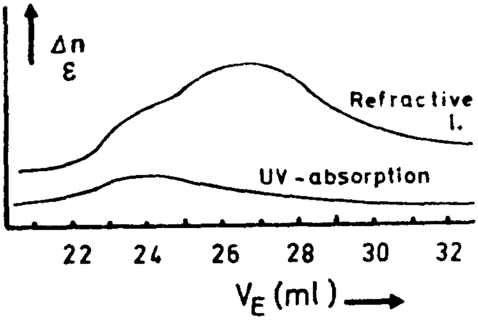

Figure 2: HPLC-GPC elution curve of TMC-POTM star block copolymer 9, UV absorption at $\lambda$ = 252 nm

## SOLUBILITY BEHAVIOUR

The investigation of the solublity of TMC and POTM, respectively, demonstrates a complex behavior caused by the semicrystallinity of the components$^{4)}$. However, an evaluation of the solubility parameters for both the homopolymers should be worthwile to judge their tendency for incompatibility.

By GEE's method$^{5)}$ three solubility parameters $\delta$ have been obtained for TMC indicating a strong dependence on the H bonding strength of the solvent: $\delta_l$ = 20.1, $\delta_m$ = 18.6 and $\delta_s$ = 21.9 (l = low, m = medium and s = strong H bonding). One $\delta$ is obtained for the non discriminating POTM ($\delta$ = 19.2 $[J^{1/2}cm^{-3/2}]$).

By HOY's increment method$^{6)}$ the solubility parameters evaluate to $\delta$ = 16.7 for TMC and to $\delta$ = 18.2 for POTM.

On the base of the solubility parameters evaluated it is likely that both polymers should be incompatible as long as no specific interaction has to be taken into account as oftenly found in cellulose derivative blends$^{7)}$. In the concerned system such specific effects seem to be ineffective: phase separation occurs in solutions of 1:1 TMC-POTM blends ($M_n$ of both components $\sim$ 100000), 5 % (w/v) in chloroform, THF and toluene. On the very contrary the incompatibility between both homopolymers seems to be distinct due to the phase separation occuring in THF which may be considered as a non selective solvent for this polymer pair.

Table II: Solubility parameters δ and H bonding class of solvents and non-solvents for TMC, POTM and TMC-POTM block copolymers (BCP). H bonding class l=low, m=medium, s=strong

| Solvent | δ $[J^{1/2}cm^{-3/2}]$ | H bonding cl. | TMC | POTM | BCP |
|---|---|---|---|---|---|
| Heptane | 15.1 | l | - | - | - |
| Diethylether | 15.1 | m | - a | + | ± e |
| Cyclohexane | 16.8 | l | - a | + | ± e |
| Methylisobutylketone | 17.2 | m | - a | + | ± e |
| Tetrachlormethane | 17.6 | l | + | + | + |
| Piperidine | 17.8 | s | - b | + | ± e |
| Toluene | 18.2 | l | ± c | + | ± e |
| Tetrahydrofuran | 18.6 | m | + | + | + |
| Ethylacetate | 18.6 | m | - a | + | ± e |
| Benzene | 18.8 | l | + | + | + |
| Chloroform | 19.0 | l | + | + | + |
| Methylethylketone | 19.0 | m | - a | + | ± e |
| Methylenchloride | 19.8 | l | + | + | + |
| 1,2-Dibromomethane | 21.3 | l | + | + | + |
| Acetophenone | 21.7 | m | - b | + | ± e |
| Pyridine | 21.9 | s | + | + | + |
| Amylalcohol | 22.3 | s | - a | + | ± e |
| Nitroethane | 22.7 | l | - a | + | ± e |
| n-Butanol | 23.3 | s | - a | + | ± e |
| Isopropanol | 23.5 | s | - a | - | - |
| Dimethylsulfoxide | 24.6 | s | - b | - | - |
| Ethanol | 26.0 | s | - | ± d | ± e |
| Methanol | 29.7 | s | - a | - | - a |
| Water | 47.9 | s | - | - | - |

a: Non-solvent, but no precipitation
b: Swelling, no precipitation
c: Molecular weight dependent. Low MW samples are dissolved badly
d: Solvent if heated
e: Solvent or swelling agent in dependence of the block copolymer composition

As demonstrated by Table II the solubility behavior of the TMC-POTM block copolymers is mainly determined by that of the TMC blocks. Only in solvents dissolving both kinds of polymers the block copolymers are soluble without restrictions. In all other cases swelling or dissolution forming opalescent solutions occur depending on the TMC content. Opalescent solutions are formed, too, when solutions of block copolymers are poured into a non-solvent of one of the blocks, e. g. ethylacetate or methanol.

## VISCOSITY BEHAVIOR

The opalescence of block copolymer solutions is caused by micell formation. But even in clear solutions of block copolymers micells can be present[8)]. This may be is the fact in solutions of TMC-POTM block copolymers in chloroform, too, as indicated by the viscosity data presented in Table I. Although viscosity information alone is unable to give quantitative information about the micells, the influence of micellization may be seen qualitatively by comparing the intrinsic viscosities of the block copolymers with those of the corresponding polymer blends. The latter can be evaluated by PHILIPOFF's formula[9]

$$[\eta]_b = \sum_i [\eta]_i \cdot x_i \qquad (5)$$

with $[\eta]_{b.i}$ the intrinsic viscosity of the blend and the i-th component, respectively, and $x_i$ the weight fraction of the i-th component.

Table III: Experimental intrinsic viscosities of TMC-POTM homopolymers, blends and block copolymers. Intrinsic viscosities of the block copolymers calculated for the corresponding blends

| Sample | | $M_n$ [Dalton] | $[\eta]_{exp}$ [l/g] | $[\eta]_{calc}$ [l/g] | POTM [%] |
|---|---|---|---|---|---|
| TMC | | 10050 | 0.058 | | 0 |
| | | 19000 | 0.102 | | 0 |
| | | 27460 | 0.152 | | 0 |
| | | 117700 | 0.520 | | 0 |
| POTM | ($M_w$) | 33690 | 0.074 | | 100 |
| | | 53380 | 0.102 | | 100 |
| | | 63100 | 0.111 | | 100 |
| | | 80360 | 0.125 | | 100 |
| | | 252000 | 0.283 | | 100 |
| Blends 1/1 | TMC<br>POTM | 19000<br>33690 | 0.078 | 0.088 | 50 |
| | TMC<br>POTM | 27460<br>80360 | 0.151 | 0.139 | 50 |
| | TMC<br>POTM | 117700<br>252000 | 0.430 | 0.402 | 50 |
| BCP 7 | TMC<br>POTM | 13000<br>11000 | 0.098 | 0.099 | 43 |
| BCP 10 | TMC<br>POTM | 27000<br>19000 | 0.165 | 0.112 | 36 |
| BCP 2 | TMC<br>POTM | 20600<br>36000 | 0.238 | 0.092 | 59 |
| BCP 6 | TMC<br>POTM | 70000<br>219000 | 0.415 | 0.273 | 56 |
| star BCP 11 | TMC<br>POTM | 27000<br>82000 | 0.195 | 0.136 | 54 |
| star BCP 8 | TMC<br>POTM | 27000<br>124800 | 0.470 | 0.157 | 64 |

For the star block copolymers a double span length is used to calculate the intrinsic viscosities, because this length only, but not the star functionality, is determining the viscosity[11].

Experimental values of intrinsic viscosities and those enumerated by the cited method are given in Table III. The [η]-M relations[10]

$$[\eta] = 1.385 \cdot 10^{-4} \cdot M_w^{.603} \qquad (6)$$

for POTM in $CHCl_3$ at $30^{\circ}$ C and[10])

$$[\eta] = 2.171 \cdot 10^{-5} \cdot M_n^{.86} \qquad (7)$$

for TMC under the same conditions have been used.

It is evident that the intrinsic viscosities of the considered three as well as of star block copolymers deviate markedly to higher values showing the stong interaction between the blocks, whereas the blends behave additive concerning the components. Light scattering studies may give more insight into the conformational situation of cellulose containing block copolymers in solution.

In consequence the behavior described of TMC-POTM block copolymers in solution is mainly governed by the incompatibility of the two different blocks. The solid state properties are determined by the incompatibility of the block components, too, as evidenced in the following paper[4]).

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