Polymer Bulletin 6, 583–588 (1982)

Polymer Bulletin

Cellulose Containing Block Copolymers

3. Solid State Properties of Trimethylcellulose – Poly(oxytetramethylene) Block Copolymers

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SUMMARY

The solid state properties of trimethylcellulose - poly(oxytetramethylene) two and star block copolymers have been investigated by IR, WAXS, polarization microscopy, DSC, and mechanic dynamical measurements. The results are in agreement with a four phase morphology consisting of an amorphous and a crystalline phase of both trimethylcellulose and poly(oxytetramethylene).

The solution properties of trimethylcellulose - poly(oxytetramethylene) block copolymers (TMC-POTM block copolymers) are governed mainly by the incompatibility of the two distinct blocks 1). In the following it is demonstrated that the incompatibility between the TMC and the POTM blocks is even more pronounced in the solid state than in solution.

IR SPECTRA

In the IR spectra of semicrystalline homopolymer POTM an absorption line occurs at 1011 cm^{-1} corresponding to skeletal bending of the crystalline POTM 2). The occurence of the same absorption line(arrow in Fig. 1) in TMC-POTM block copolymers with > 50% POTM content shows that a crystalline POTM phase is present. In the IR spectra of TMC-POTM block copolymers with < 50% POTM content the line at 1011 cm^{-1} is overlaped by the very broad C-O streching band of the TMC blocks.

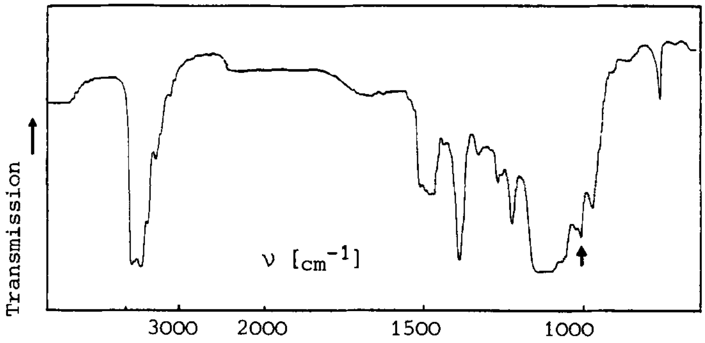

Figure 1. IR spectra of TMC-POTM block copolymer 9 1) (64% POTM)

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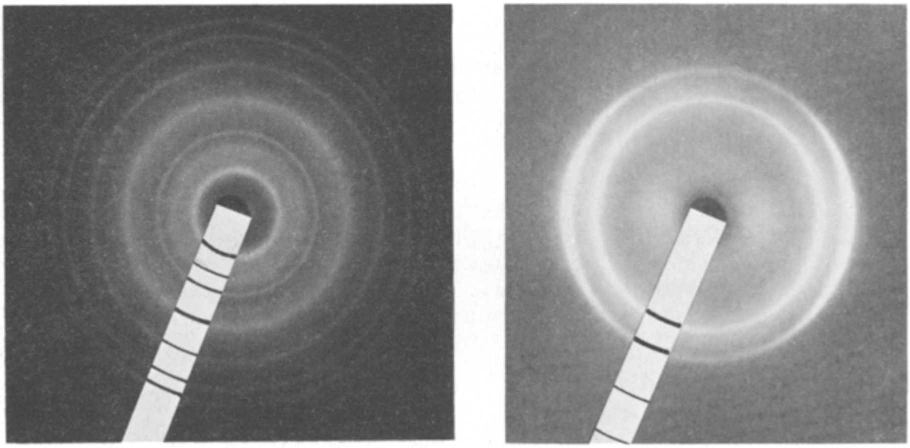
WIDE ANGLE X-RAY SCATTERING

Fig. 2 shows DEBYE - SCHERRER diagrams($Cu_{K\bar{\alpha}}$) of the semicrystalline homopolymers,TMC and POTM. It can be seen that TMC shows



TMC POTM

Figure 2: DEBYE - SCHERRER diagrams of TMC and POTM

characteristic reflexes at $\theta < 10^{o}$ [3] whereas all the POTM reflexes are at $\theta > 10^{o}$ [2]. The WAXS investigation of the TMC-POTM block copolymers shows that in all the samples TMC crystallites are present(Fig. 3). In TMC-POTM block copolymers with POTM block molecular weights > 15.000 dalton POTM crystallites are coexistent. The higher the block molecular weights the

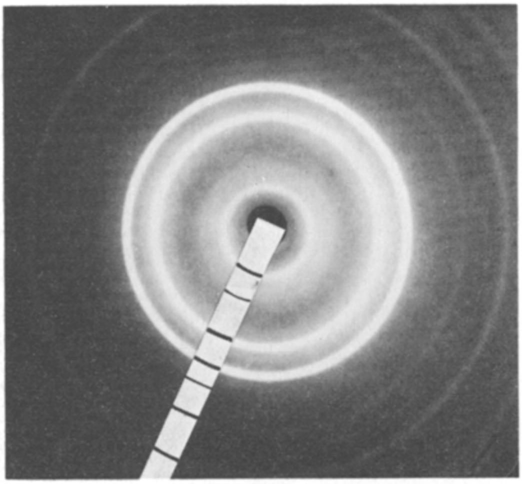


Figure 3: WAXS diagram of TMC-POTM block copolymer 5 [1]

more reflexes occur, because the phases are more distinct. The possition of the reflexes is not changed when compared to the homopolymers indicating that the crystal structures in the block copolymers are identical with those of the homopolymers.

POLARIZATION MICROSCOPY

Whereas cellulose derivatives though semicrystalline normally do not exhibit spherulites [4] POTM forms spherulites even in block copolymers [5]. In our case all investigated TMC-POTM two block copolymers show up spherulites. This is surprising because in corresponding TMC-POTM blends the spherulite growth of the POTM is strongly influenced by the presence of TMC [6]: only blends with < 10% TMC show regular POTM spherulites. Higher TMC contents disturb the spherulite growth remarkable(Fig. 4) and at 70% TMC the spherulite formation is completely hindered. The spherulites formed by the TMC-POTM two block copolymers are well developed(Fig. 5) but show different sizes due to non uniform nucleation kinetics. TMC-POTM star block copolymers behave completely different(Fig. 6): only small crystallites occur

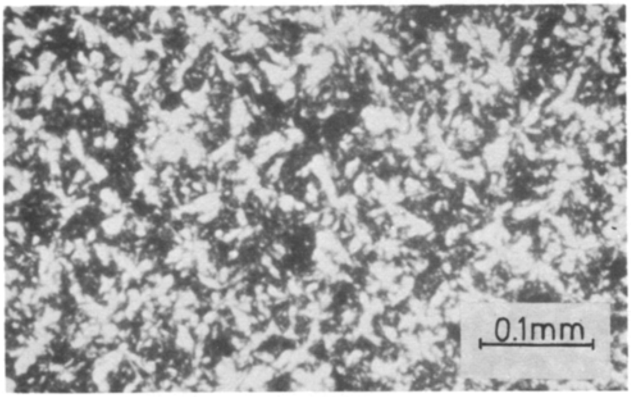


Figure 4: POTM crystallites formed by a TMC-POTM blend(53% TMC)

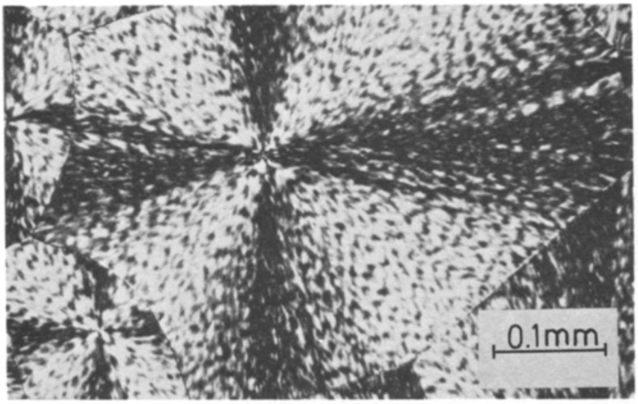


Figure 5: POTM spherulite formed by TMC-POTM two block copolymer 5

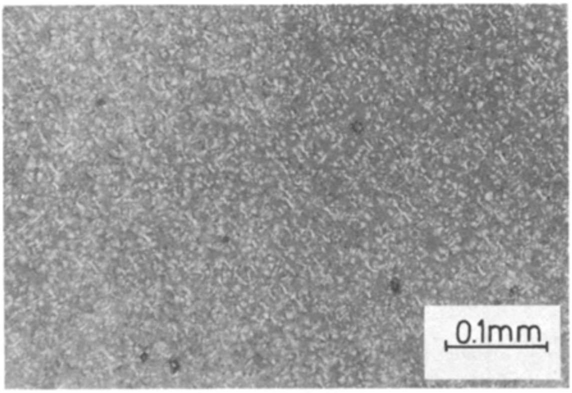


Figure 6: POTM crystallites formed by TMC-POTM star block copolymer 9

which are formed very slowly. The central linkage of the POTM blocks by the poly(4-vinylpyridine) 7) seems to hinder the diffusion of the chains and thus supress spherulite growth.

DSC MEASUREMENTS

Fig. 7 shows the DSC diagrams of POTM homopolymer, a TMC-POTM two block copolymer, and a TMC-POTM star block copolymer. It can be seen that the melting temperature of the POTM crystallites in the block copolymers is nearly independent of the block copolymer composition but is about 4°C lower than the melting temperature of the homo POTM crystallites. This could be explained assuming 8) that the rigid TMC matrix hinders the formation of the thermodynamically favored crystallite size formed under the same conditions in the homo POTM.

Similar results for the TMC crystallites can not be obtained because the sample decomposes before reaching the TMC melting point.

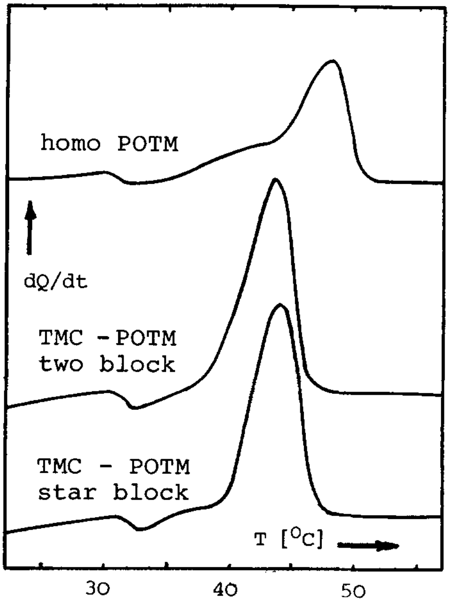
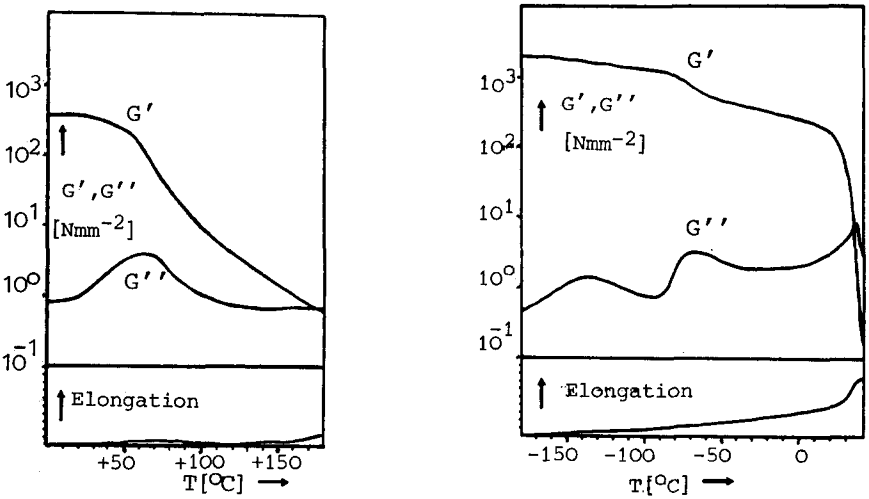


Figure 7: DSC spectra of homo POTM, TMC-POTM two block copolymer 10, and TMC-POTM star block copolymer 9

TORSION PENDULUM SPECTRA

Fig. 8 shows torsion pendulum spectra of homo TMC, a TMC-POTM



homo TMC

TMC-POTM two block

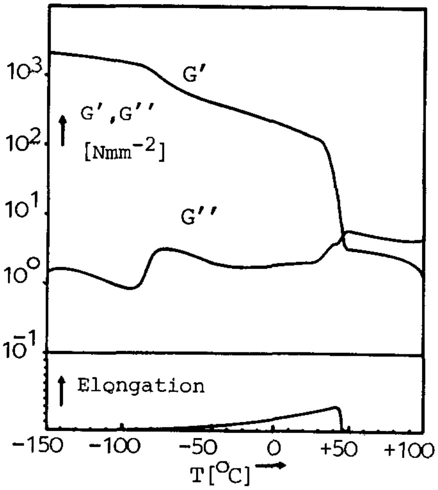


Figure 8. Torsion pendulum spectra (frequency 1 Hz, tensile stress 3,6 p) of homo TMC(sample thickness 0.2 mm), TMC-POTM two block copolymer 5(thickness 1.1 mm), and TMC-POTM star block copolymer 9(thickness 1.05 mm)

two block copolymer, and a TMC-POTM star block copolymer. The TMC sample cast from solution (CH_2Cl_2) yields a broad glass transition at about 80°C. The spectra of TMC-POTM two block copolymers are identical with spectra for homo POTM 9): below the melting point of the POTM crystallites (43°C) the sample is crosslinked physically. Above this temperature the sample flows. The TMC-POTM star block copolymers are crosslinked as expected even above the POTM melting temperature. Thus the torsion pendulum spectra show the characteristics of both the homopolymer semicrystalline POTM and the homopolymer semicrystalline TMC.

CONCLUSION

The discussed results lead to the following conclusions: The morphology of the TMC-POTM block copolymers consists of four well separated phases, an amorphous and a crystalline phase of both TMC and POTM. However, a crystalline POTM phase can not be observed if the POTM block molecular weight is < 15.000 Dalton. The TMC-POTM star block copolymers are effectively crosslinked but due to the decomposition of the samples they are not processable thermoplastically.

ACKNOLEDGEMENT

Financial support by the BUNDESMINISTERIUM FÜR FORSCHUNG UND TECHNOLOGIE gratefully is acknowledged.

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Received and accepted February 8, 1982