Macromol. Symp. ***183****, 121–126 (2002)*

Well-defined Crosslinked Materials via Ring Opening Metathesis Polymerisation

Ezat Khosravi

IRC in Polymer Science and Technology, Durham University, Durham,
DH1 3LE, UK

Summary: The work reported here is part of our ongoing programme of work directed towards the synthesis and characterisation of polymeric materials via ROMP-RIM and ROMP-RTM. It describes the synthesis and characterisation of well-defined linear and crosslinked polymeric materials via ROMP-RTM. The process involves in-mould polymerisation of monofunctional imidonorbornene monomers, with different alkyl side chain lengths, to give a range of linear polymers. The process also involves in-mould copolymerisation of monofunctional imidonorbornene monomers, with different alkyl side chain lengths and difunctional monomers with different alkylene spacer lengths, to produce well-defined crosslinked polymers. The glass transition temperature (T_g) of the linear polymers was found to depend on the length of the alkyl side chain. For the crosslinked materials the results show that as the percentage of the difunctional, crosslinking unit, is increased (1, 5 and 10 molar percentage of the difunctional monomer) the glass transition shifts to a higher temperature, the height of the tanδ peak decreases and the plateau shear modulus above T_g increases. These results are as expected for an increase in the crosslink density of a polymer.

Introduction

The olefin metathesis has made remarkable strong developments with an incredible speed in various directions. New catalyst systems have been developed which have resulted in the synthesis of novel materials. Other fascinating developments have been the new catalysts for stereoselective metathesis and catalysts with considerable functional group tolerance. These new catalysts in addition to Ring Opening Metathesis Polymerisation (ROMP) and Acyclic Diene Metathesis (ADMET) are now powerful tools for Ring Closing Metathesis (RCM) and have found many applications in the synthesis of natural products. A lot of information has been established about all aspects of the olefin metathesis and there is a vast literature concerning the process, covering the initiators, mechanistic features and applications of this reaction in organic and polymer synthesis.[1,2]

We demonstrated that well-defined initiators allow the control of many aspects of the process, including *cis/trans* vinylene content and tacticity as well as molecular weight and its distribution.[3,4] These living ROMP reactions have been shown to result in the synthesis of a variety of interesting polymers such as stereoregular fluoropolymers,

CCC 1022-1360/00/$ 17.50+.50/0

block copolymers and stereo-block copolymers.[5,6] We also combined living ROMP and living anionic polymerisation to synthesise well defined comb-graft copolymers. This technique allows the control of the lengths of the grafts and the backbone chains through the use of the two living polymerisation methods.[7,8] The advances achieved, during the last few years, in the design of ROMP initiators which are tolerant towards polar functional groups (aldehydes, acids, alcohols) and aqueous environments have provided the polymer community with access to a wide range of functional polymers not previously available. This major achievement has opened up a number of technological possibilities in the area of novel functional materials, such as water-soluble polymers, polar polymers and biocompatible materials.[1,2] Here we report the synthesis and characterisation of well-defined linear and crosslinked polymeric materials by ROMP in resin transfer moulding processing (RTM).

Resin Transfer Moulding - ROMP Processing

Dicyclopentadiene, DCPD, is cheap and can be polymerised by ROMP, which yields a crosslinked polymer. This polymerisation process can be tailored to have the characteristics which make it readily adaptable to either reaction injection moulding (RIM) or RTM. The production of large moulded objects from DCPD-based feeds using RIM technology was developed mainly in the USA by BF Goodrich under the trade name TELENE and by Hercules under the trade name METTON. The catalysts used in METTON process is based on a combination of $WCl_6/WOCl_4$ and nonylphenol with Et_2AlCl. In the TELENE process the preferred catalyst is based on trialkylammonium molybdates and Et_2AlCl. The advantages of DCPD include a rapid reaction and good product mechanical properties. The disadvantages include a nasty smell, an exothermic reaction, which can be difficult to control, and the difficulty of regulating the crosslinking reaction, which reduces the processability and the range of mechanical properties available. Nevertheless, poly(DCPD) is an interesting material and is finding market applications, as evident by the number of published papers and patents.[9-15]

A major motivation for this work was a desire to synthesise alternative monomers to DCPD for RIM and RTM applications. The process that we have developed is very simple and involves in-mould polymerisation of monofunctional monomers to give a range of linear polymers. It also involves in-mould copolymerisation of monofunctional monomers with difunctional monomers to produce well-defined crosslinked polymers.

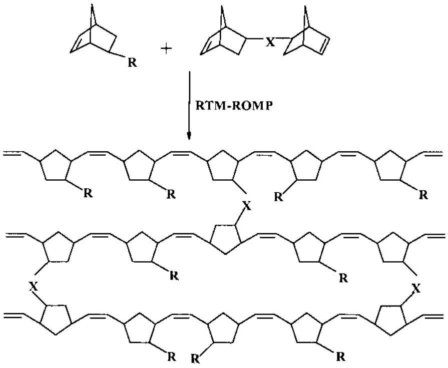
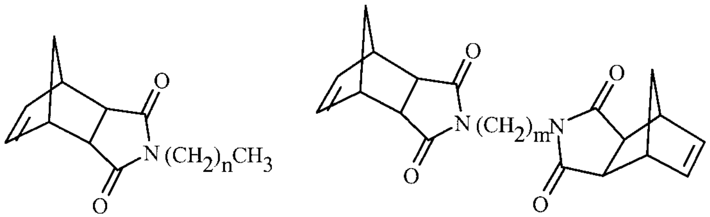


Figure 1. Reaction Scheme for RTM-ROMP processing

A crucial factor in the development of the synthesis route was the availability of the ruthenium initiator , $Cl_2Ru(=CHPh)((PC_6H_{11})_3)_2$, developed by Grubbs et al.[16-19] N-alkyldicarboxyimidonorbornenes, termed CnM, carrying pendant alkyl chains of different lengths (n=3,4,5) (Figure 2a) and bis(N-alkylenedicarboxyimidonorbornenes) , termed CmD, with an alkylene spacer (m=3,5,6,9,12) (Figure 2b) were used as monofunctional and difunctional monomers respectievely.[4,20-22] Monofunctional N-alkyldicarboxyimidonorbornenes were polymerised using RTM-ROMP processing to give linear polymers. The difunctional bis(N-alkylenedicarboxyimidonorbornenes) were co-polymerised with the monofunctional monomers to produce crosslinked polymers using the same processing method.



a) Monofunctional monomer - CnM
n= 2-9 and 12

b) Difunctional monomer - CmD
m= 3,5,6,9 and 12

Figure 2. The chemical structures of mono- and di-functional N-alkyl dicarboxyimidonorbornene monomers.

Mechanical Properties of Linear Polymers (PolyCnM)

The results showed that the optimum Monomer : Initiator ratio for the C6M system was 4000:1. Figure 3 shows a comparison of the dynamic torsion results (measured at a frequency of 1 Hz) for polyCnM materials with n=4, 5 and 6. It can be seen that the shape of the curves is very similar, but that the glass transition temperature, T_g, falls with increasing alkyl side chain length, due to internal plasticisation.

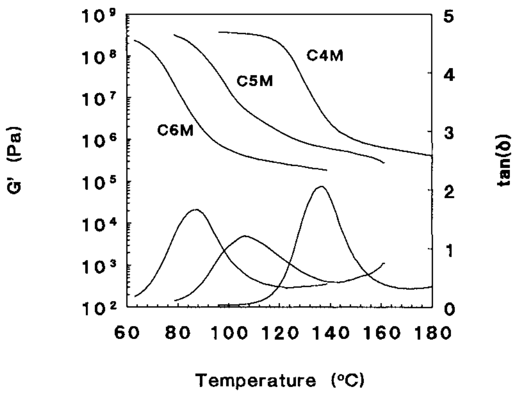


Figure 3. Torsion modulus G' and tanδ versus temperature for polyC4M, polyC5M and polyC6M.

Table1. The mechanical properties of the linear polymers

Polymer	T_g (°C)	Density kg/m^3	Modulus (20°C) (Gpa)	Yield Strength (20°C) (Mpa)
C4M	136	1150	2.36	67.4 ± 5.7
C5M	106	1100	1.53	60.4 ± 2.1
C6M	87	1100	1.46	42 ± 2.0

Some preliminary mechanical properties were measured for the polyC4M, polyC5M and polyC6M and the results are shown in Table 1. The polyC4M had the highest density at 1150 kg/m^3, with the other two polymers showing a similar density of 1100 kg/m^3. The room temperature modulus was found to fall with increasing side chain length, a consequence of the different temperature differences between room temperature (20°C) and T_g for the three polymers, as mentioned earlier. Three point bend measurements showed that the yield stress fell with increasing side chain length, with an accompanying change from brittle to ductile behaviour. A much more detailed study of the effect of the side chain length on deformation behaviour will form the basis of future studies.

Mechanical Properties of Crosslinked Polymers (CnM+ x% CmD)

The results showed that the optimum Monomer : Initiator ratio for the C5M/CmD system was 8000:1. Having established this fact, a range of samples was prepared using this ratio, to investigate the effect of varying the percentage of the difunctional component, and the length of the difunctional linkage. Figure 4 shows the dynamic shear modulus results for the C5M/C12D combination, with 1, 5 and 10 molar percentage of the difunctional component. The results show that as the percentage of the difunctional, crosslinking unit, is increased the glass transition shifts to a higher temperature, the height of the tanδ peak decreases and the plateau shear modulus above T_g increases. These results are as expected for an increase in the crosslink density of a polymer.

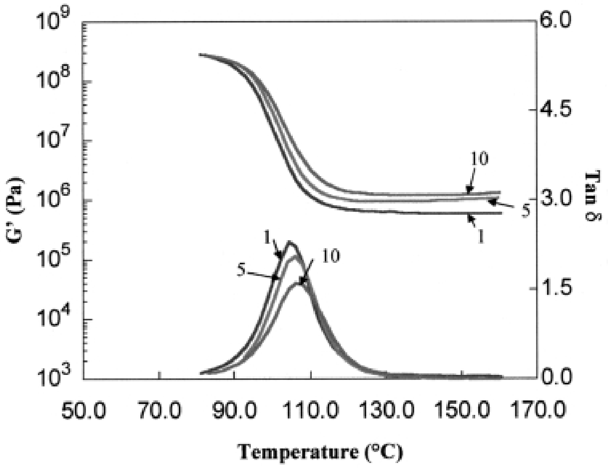


Figure 4. Dynamic torsion results for C5M + x molar percent of C12D: x=1, 5 and 10.

Table 2 shows measured mechanical properties for the crosslinked materials and compares them with bis-phenol-A-polycarbonate and Poly(DCPD), TELENE. The room temperature moduli and ultimate bending strength of the crosslinked materials are, in general, higher than the equivalent thermosetting materials. Of particular interest are the high values for yield strength and toughness, which are comparable to known 'high toughness' materials such as polycarbonates.

Table 2. The mechanical properties of the crosslinked materials

Polymer	T_g (°C)	Density kg/m^3	Modulus (20°C) (Gpa)	Strength (20°C)(Mpa)
C4M/2%C12D	~120	1150	2.36±0.2	61 ± 15(F)
C5M/2%C12D	106	1100	1.53±0.2	72 ±2 (Y)
C6M/2%C12D	87	1100	1.46±0.1	59 ±3 (Y)
Polycarbonate	150	1200	2.3	62 (Y)
Poly(DCPD) TELENE 1100	145	1030	1.9	45

[1] R. H. Grubbs, E. Khosravi, In *Synthesis of Polymers - a Volume of Materials Science and Technology Series*; Schluter, A. D., Ed.; Wiley-VCH: **1998**, p 63-104.

[2] E. Khosravi and T. Szymansk-Buzar, "ROMP and related chemistry: state of the art and visions for the new century", NATO ASI Series, Kluwer Academic Publishers, in print.

[3] G. C. Bazan, E. Khosravi, R. R. Schrock, W. J. Feast, V. C. Gibson, M. B. Oregan, J. K. Thomas, W. M. Davis, *J. Am. Chem. Soc.*, **1990**, *112*, 8378.

[4] E. Khosravi, A. A. Al-Hajaji, *Polymer,* **1998**, *39*, 5619.

[5] E. Khosravi, In *Modern Fluoropolymers, High Perfomance Polymers for Diverse Applications*; Scheirs, J., Ed.; Wiley & Sons: **1997**, p Chapter 8.

[6] W. J. Feast, E. Khosravi, *J. Fluor. Chem.*, **1999**, *100*, 117.

[7] W. J. Feast, V. C. Gibson, A. F. Johnson, E. Khosravi, M. A. Mohsin, *Polymer,* **1994**, *35*, 3542.

[8] A. C. M. Rizmi, E. Khosravi, W. J. Feast, M. A. Mohsin, A. F. Johnson, *Polymer,* **1998**, *39*, 6605.

[9] R. J. Minchak, US Patent 4,426,502, issued 17/01/**1984**.

[10] R. H. Grubbs, L. K. Johnson, S. T. Nguyen, US Patent No. 5,312,940, issued 5/17/**1994**.

[11] R. H. Grubbs, L. K. Johnson, S. T. Nguyen, US Patent No. 5,342,909, issued 8/30/**1994**.

[12] R. H. Grubbs, S. T. Nguyen, L. K. Johnson, US Patent No. 5,710,298, issued 1/20/**1998**.

[13] R. H. Grubbs, Jr. C. S. Woodson, US Patent No. 5,728,785, issued 3/17/**1998**.

[14] Jr. C. S. Woodson, R. H. Grubbs, US Patent No. 5,939,504, issued 8/17/**1999**.

[15] A. Bell, *Polym. Preprints, **1994**, 35, 694.*

[16] S. T. Nguyen, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc., **1993**, 115, 9858.*

[17] P. E. Schwab, M. B. France, J. W. Ziller and R. H. Grubbs, *Angew. Chem., Int. Ed. Engl., **1995**, 34, 2039.*

[18] P. E. Schwab, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc., **1996**, 118, 100.*

[19] M. Hillmeyer, W. R. Laredo, R. H. Grubbs, *Macromolecules, **1995**, 28, 6311.*

[20] E. Khosravi and A. A. Al-Hajaji, *Eur. Polym. J., **1998**, 34, 153.*

[21] E. Khosravi, W. J. Feast, A. A. Al-Hajaji and T. J. Leejarkpai, *Mol. Catal. A: Chemical, **2000**, 160, 1.*

[22] P. J. Hine, T. Leejarkpai, E. Khosravi, R. A. Duckett and W. J. Feast, *Polymer, **2001**, 42, 9413.*