# Functional oligomerization of dicyclopentadiene

**Valérie Heroguez, Alain Soum and Michel Fontanille***
*Laboratoire de Chimie des Polymères Organiques (URA CNRS), ENSCPB, Université Bordeaux-1, 351 cours de la Libération, 33405 Talence Cedex, France*
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Whilst the $[WCl_6/SnMe_4]$ initiating system leads to crosslinked polymers of dicyclopentadiene (DCP), a quasi-selective metathetic process can be carried out with $[W(OAr)_2Cl_4/SnMe_4]$ as initiator to obtain soluble poly(DCP). The control of molar masses is carried out by transfer to acyclic olefins. By using unsaturated diesters as transfer agents, difunctional oligomers are obtained. The quantitative reduction of ester end groups leads to hydroxy-ended oligomers which could be used for chain extension by diisocyanate.

**(Keywords: polydicyclopentadiene; metathesis polymerization)**

## *Introduction*

Metathesis catalysts generally act on the two unsaturated cycles of dicyclopentadiene (DCP) leading to crosslinked networks. This phenomenon has been exploited to prepare new materials that can be processed by reaction injection moulding (RIM)[1]. Recent studies by Boutarfa *et al.*[2] and Leconte[3] show that a mainly linear polymerization of DCP can be obtained simultaneously with high catalytic activity. Nevertheless, part of the polymer produced has a crosslinked structure and precipitates in the reaction medium. To avoid this phenomenon, Boutarfa *et al.*[2] and Leconte[3] suggested adding small amounts of an acyclic olefin to the reaction medium; this additive acts as a transfer agent and, by lowering the molar masses of the system, lowers the probability of network formation. This method was used by Reyx *et al.*[4] to produce oligomers from 1,5-cyclooctadiene.

The aim of this study was to use functional transfer agents during the polymerization of DCP, in order to simultaneously obtain a reduction in chain length (and of crosslink formation) and the functionalization of chain ends. To that end, various transition metal-based catalytic systems were studied; the best results were obtained with tungsten-based catalysts and only the corresponding results will be presented in this paper.

## *Experimental*

*Chemicals.* Hex-3-ene-1,6-methyldioate was synthesized by esterification of hex-3-ene-1,6-dioic acid as previously described[4]. DCP (Aldrich) was distilled twice: first over sodium under reduced pressure and then by cryo-distillation under vacuum from a sodium mirror. It is an exo/endo mixture with ~10% exo compound. Toluene was distilled over sodium. Hex-1-ene was dried over molecular sieves. $W(OAr)_2Cl_4$ was obtained by reacting $WCl_6$ with 2,6-dichlorophenol as described in reference 5.

*Polymerizations* were performed under argon atmosphere by introducing successively initiator, solvent, internal standard, DCP, transfer agent and co-initiator, in a flask equipped with a septum. The reaction medium was stirred with a magnet. The reaction was followed by chromatographic titration of residual monomer against time. The reaction medium was filtered on sintered glass; oligomers were precipitated in methanol, recovered by filtration and dried under vacuum.

*Characterization.* Molar masses were determined by s.e.c. (polystyrene calibration). Ester functions content was measured by $^1H$ n.m.r. By a combination of the number average molar mass ($\bar{M}_n$) and ester group concentration it is possible to obtain the average functionality $\bar{f}$. The glass transition temperature ($T_g$) was measured by d.s.c. on a Mettler TA 3000 calorimeter (heating rate $10°C\ min^{-1}$). $^1H$ and $^{13}C$ n.m.r. spectra were obtained at 250 and 62.25 MHz, respectively, in $CDCl_3$ ($50\ g\ l^{-1}$), at room temperature, on a Bruker AC 250 spectrometer.

## *Results and discussion*

A first series of experiments were performed in order to compare the $[WCl_6/SnMe_4]$ conventional system to $[W(OAr)_2Cl_4/SnMe_4]$ (with $Ar = 2,6\text{-}C_6H_3Cl_2$) proposed by Boutarfa *et al.*[2].

For both systems, the activity and the selectivity of the process were compared. In both cases, experiments were conducted up to complete conversion of monomer (measured by v.p.o.) and under similar conditions, i.e. toluene as solvent, $T = 60°C$, $[DCP]_0 = 0.30\ M$, $[DCP]_0/[W(OAr)_2Cl_4] = 30$ and $[SnMe_4]/[W(OAr)_2Cl_4] = 2$.

*Initiation by* $[WCl_6/SnMe_4]$. Complete monomer conversion was obtained within a few minutes, thus indicating that the activity of the system is high. It is also observed that the selectivity of the process is low; indeed, in the reaction conditions given below, the soluble polymer yield was only ~50%, the rest being in the state of cross-linked gel.

The s.e.c. analysis of the soluble fraction shows a bimodal distribution of the polymeric species (*Figure 1A*). By $^1H$ n.m.r. spectrometry, it is possible to measure the relative concentration in saturated and in unsaturated monomeric units. The ratio $[H_{sat}]/[H_{ethylenic}]$ is 2.6 (instead of 2.0 for a pure metathesis polymerization) showing that a relatively important fraction seems to

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* To whom correspondence should be addressed

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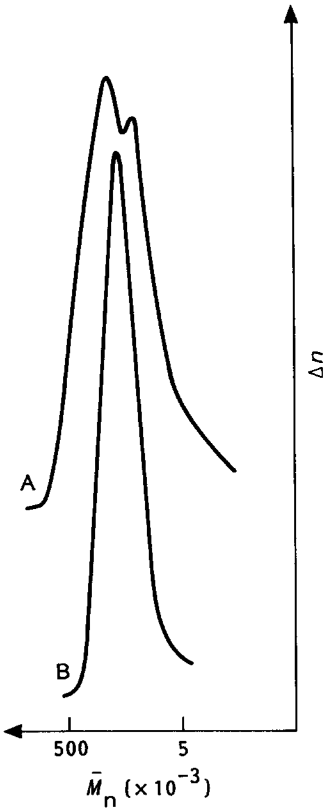

**Figure 1** Size exclusion chromatograms of poly(DCP) prepared with different initiating systems: (A) with $WCl_6/SnMe_4$, (B) with $W(OAr)_2Cl_4/SnMe_4$

react by addition to the double bond, probably by a cationic process initiated by $WCl_6$.

*Initiation by* [$W(OAr)_2Cl_4/SnMe_4$]. With this initiating system, the activity is clearly lower than that of the previous system; indeed, complete monomer conversion was obtained within $\sim$3 h. Nevertheless, this activity is compatible with the production of relatively large amounts of products.

Concerning the selectivity of the process, the use of the above-mentioned conditions allows the preparation of a totally soluble polymeric material. But increase in either monomer concentration or initiator concentration leads to the partial formation of a crosslinked gel, swollen in the reaction medium, which can be eliminated by filtration.

The analysis of the product resulting from the homogeneous (soluble) polymerization shows that: the s.e.c. chromatogram is monomodal (*Figure 1B*); the $^1H$ n.m.r. spectrum corresponds to polymers resulting only from metathetic polymerization, more probably of the norbornene-like ring ($[H_{sat}/H_{unsat}]$ is 2.0).

The ability of the system to generate oligomers in the presence of transfer agents, was also checked. A series of experiments were performed with hex-1-ene as a transfer agent. *Figure 2A* shows the effect of the ratio of [transfer agent]/[DCP] ($[DCP]_0$ being constant) on $\bar{M}_n$ of poly(DCP). The lowering of the molar masses by the transfer process is corroborated by the presence of two peaks at 114 and 140 ppm in the $^{13}C$ n.m.r. spectrum of the oligomers (these peaks correspond to ethylenic end groups). It is important to note that the transfer reaction is not first order in hex-1-ene, thus indicating a complex reaction scheme. Moreover, the relatively low value of $\bar{M}_n$ observed in the absence of transfer agent suggests that, due to the long reaction time, a back-biting process might provoke an additional limitation of the molar masses. As expected, s.e.c. chromatograms are monomodal.

In order to prepare functional oligomers, hex-1-ene was replaced by hex-3-ene-1,6-methyldioate, a compound which was selected as an efficient transfer agent in the functional oligomerization of norbornene[5]. As with hex-1-ene, the transfer reaction is not first order with respect to unsaturated diester (*Figure 2B*) and the detailed mechanism of the corresponding process is probably complex. Depending on the ratio of $[\text{diester}]_0/[DCP]_0$, it is possible to obtain oligomers whose $\bar{M}_n$ varies from $\sim 29 \times 10^3$ to $1.6 \times 10^3$ g $mol^{-1}$ (*Figure 2B*). The s.e.c. trace is monomodal.

Structural analysis by $^1H$ n.m.r. allows the determination of the ester chain ends concentration (*Figure 3A*), and by combination with $\bar{M}_n$ the average functionality $\bar{f}$ can be obtained.

*Table 1* gives the results of experiments performed with relatively high concentrations of diester and producing low molar mass oligomers. For such oligomers, the accuracy of chain-end titration is good and the validity of the s.e.c. determination of $\bar{M}_n$ was checked by tonometry. The agreement is satisfactory and the accuracy for the average functionality $\bar{f}$ can be estimated to be $\sim$0.2.

The reduction of ester end groups into hydroxy functions was performed as previously described by Cramail *et al.*[6]. Dihydroxytelechelic oligomers were obtained quantitatively and the corresponding characterization was carried out by $^1H$ n.m.r. A corresponding spectrum is given in *Figure 3B*.

As expected, s.e.c. analysis of reduced samples shows

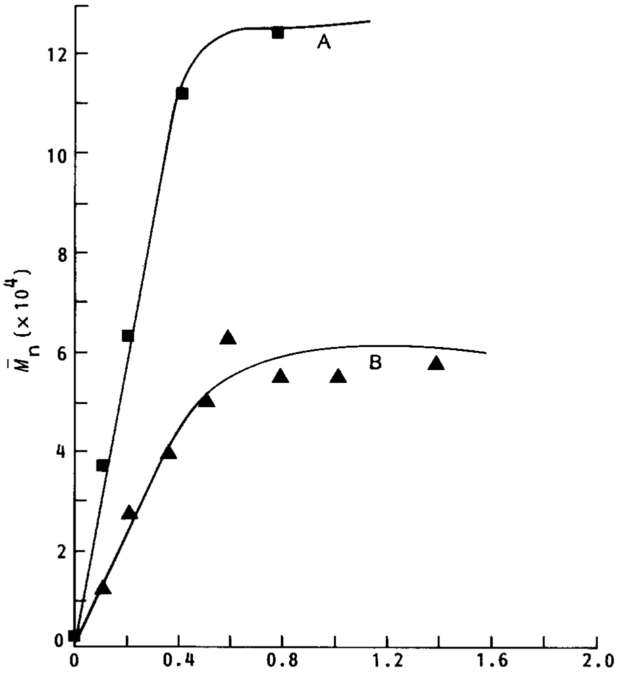

**Figure 2** Effect of the ratio $r$ of the [transfer agent]/[DCP] on $\bar{M}_n$ of poly(DCP). [DCP] = 0.19 M, $[W(OAr)_2Cl_4] = 6 \times 10^{-3}$ M, $[SnMe_4]/[W(OAr)_2Cl_4] = 2$: (A) with hex-1-ene; (B) with hex-3-ene-1,6-methyldioate

**Table 1** Structural and thermal characteristics of poly(DCP) oligomers prepared in the presence of variable concentrations of hex-3-ene-1,6-methyldioate

| $r$ = [diester]/[DCP] | [diester] (mol $l^{-1}$) | $\bar{M}_n$ (by g.p.c.) | $\bar{M}_n$ (by v.p.o.) | $I_{CH_3O}/I_{H_{ethylenic}}$ | $\bar{f}$ | $T_g$ (°C) |
|---|---|---|---|---|---|---|
| 0.5 | 0.09 | 2000 | — | 0.10 | 2.0 | — |
| 0.6 | 0.11 | 1600 | — | 0.10 | 1.7 | — |
| 0.8 | 0.15 | 1800 | — | 0.10 | 2.0 | — |
| 1.0 | 0.20 | 1800 | 1780 | 0.10 | 2.0 | 70 |
| 2.0 | 0.38 | 1600 | 1500 | 0.12 | 1.8 | 75 |

[DCP] = 0.19 M, $[W(OAr)_2Cl_4] = 6 \times 10^{-3}$ M, $[SnMe_4]/[W(OAr)_2Cl_4] = 2$

that the reduction process does not modify the molecular dimensions of the chains since $\bar{M}_n$ remains unchanged.

The determination of the $T_g$ by d.s.c. is difficult, due to the very small variation in the heat capacity observed for the samples studied. Nevertheless, the $T_g$ of DCP oligomers was found to be significantly lower (*Table 1*) than that of the corresponding high polymer ($T_g$ = 130°C)[7].

Thus, it seems that the crosslinking of DCP polymers is mainly due to the metathesis of the double bonds, this process acting preferably on the norbornene-like cycle. The use of initiators unable to induce a cationic process can allow soluble polyalkenamers to be obtained. The corresponding systems are able to lead to functional oligomers by transfer to a difunctional acyclic olefin.

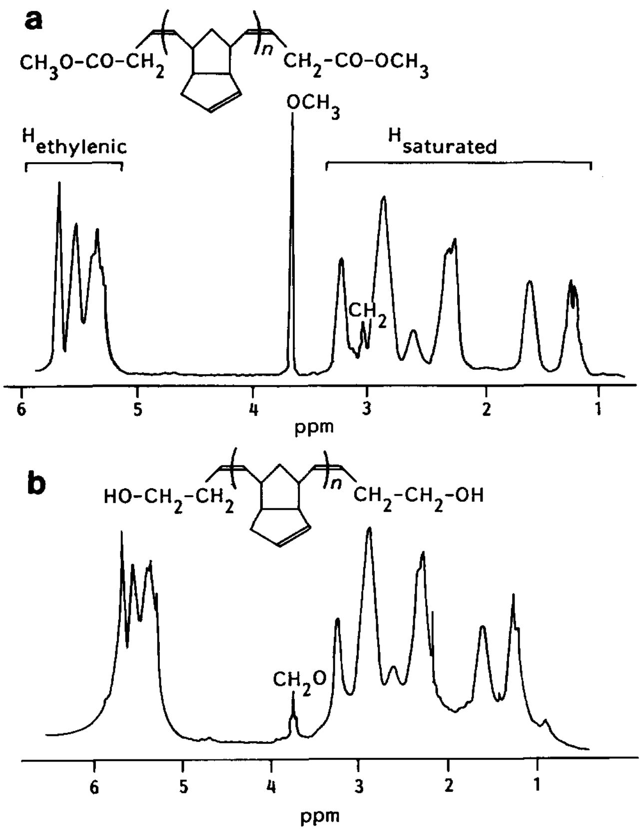

**Figure 3** $^1$H n.m.r. spectra of oligomers of DCP obtained in the presence of hex-3-ene-1,6-methyldioate: (a) before reduction; (b) after reduction

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