Chinese Chemical Letters Vol. 14, No. 3, pp 245 – 246, 2003
http://www.imm.ac.cn/journal/ccl.html

Reverse Atom Transfer Radical Polymerization of (-)-Menthyl Methacrylate

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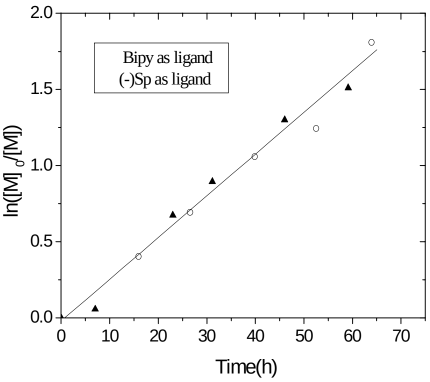
Abstract: The reverse atom transfer radical polymerization(RATRP) of (-)-menthyl methacrylate ((-)-MnMA) with AIBN(AIBN/$CuCl_2$/bipyridine(bipy) or (-)sparteine((-)Sp) =1/2/4) initiating system in THF has been studied. The dependence of the specific rotation on molecular weight was investigated.

Keywords: Reverse atom transfer radical polymerization, menthyl methacrylate, specific rotation.

ATRP has grown rapidly in recent years[1]. Reverse ATRP has been explored since 1995[2,3], and in this process, a higher oxidation state transition-metal species $Mt^{n+1}X/L_x$ and a conventional radical initiator were used instead of a lower oxidation state $Mt^{n}X/L_x$ and halide species RX respectively. However, chiral bulky monomers have not been studied by this method so far. In this communication, (-)-MnMA was synthesized[4] and polymerized by RATRP with an AIBN/$CuCl_2$/bipy or (-)Sp initiating system, which was heterogeneous and homogeneous system respectively, and the specific rotation of polymers was investigated. The polymerization was carried out in a predried glass ampule under argon[5].

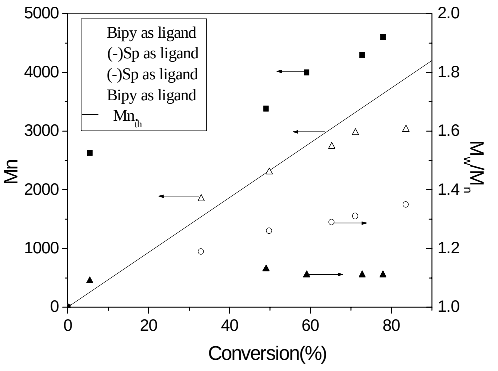
As shown in **Figure 1**, linear first-order kinetic plots were observed when bipy or (-)Sp was used as ligand, indicating that the number of active species remained constant during the polymerization. As shown in **Figure 2**, **t**he molecular weights of polymers increased linearly with conversion, but were much higher than calculated ($Mn._{th}$) for bipy as ligand, and derivated calculated ones at higher conversion for (-)Sp as ligand. The deviation of $Mn._{GPC}$ from $Mn._{th}$ may be partially due to the differences in the hydrodynamic volume of poly((-)-MnMA) and polystyrene standards used to calibrate the GPC, or the inefficient initiation that presumably caused by slow deactivation, or some chain transfer reactions. The polydispersities of polymers remained quite low(Mw/Mn <1.35) throughout the reaction. The dependence of the specific rotation values of poly((-)-MnMA)s on molecular weight($Mn._{GPC}$) was shown in **Figure 3**, indicating that the specific rotation values almost remained as that of the monomer($[\alpha]_D^{20}$ -91.8).

Figure 1 Kinetic plots for the ATRP of (-)-MnMA using THF as solvent.



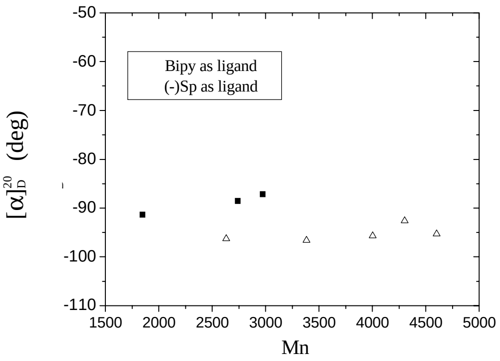
Conditions: 80°C; [(-)-MnMA]=0.63mol/L, [AIBN]=1/2[$CuCl_2$]=1/4[bipy]=0.012mol/L; [(-)-MnMA]=0.52 mol/L, [AIBN] =1/2[$CuCl_2$]=1/4[(-)-Sp]=0.022mol/L.

Figure 2 Dependence of molecular weight, $Mn._{GPC}$, and molecular weight distribution, Mw/Mn, on monomer conversion for the ATRP of (-)- MnMA.



See **Figure 1** for conditions.

Figure 3 Dependence of specific rotation(c=0.4, THF) on molecular weight($Mn._{GPC}$) for poly-((-)-MnMA).



See **Figure 1** for conditions

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Received 8 May, 2002