

Controlled/"Living" Radical Polymerization of (-)-Menthyl Methacrylate

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Abstract: The atom transfer radical polymerization(ATRP) of (-)-menthyl methacrylate((-)-MnMA) mediated by CuCl/bipyridine and ethyl 2-bromopropionate or 1-phenylethyl bromide in THF system has been studied. The dependence of the specific rotation on molecular weight and the CD of Poly((-)-MnMA) thus obtained was investigated.

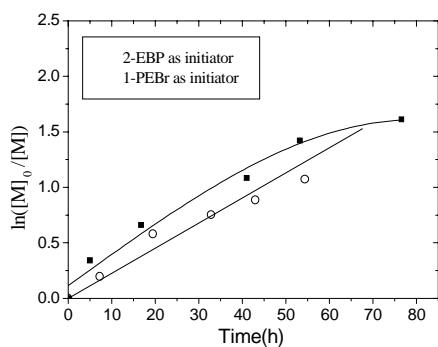
Keywords: Controlled polymerization, menthyl methacrylate, specific rotation.

Research on controlled/"living" radical polymerization has grown rapidly in recent years. One of the most successful systems is atom transfer radical polymerization (ATRP). Though a great deal of literatures has been published in recent years regarding the application of ATRP to a variety of methacrylates under various conditions¹, to our best knowledge, chiral bulky methacrylates have not been studied by this method. In this communication, (-)-MnMA was synthesized² and polymerized by ATRP, and the chiroptical properties of polymers were investigated. The polymerization was carried out in a dry glass ampule under argon³. Ethyl 2-bromopropionate(2-EBP) or 1-phenylethyl bromide(1-PEBr) and CuCl/bipyridine(bpy) was used as initiator and catalyst respectively.

As shown in **Figure 1**, linear first-order kinetic plots were observed when 2-EBP or 1-PEBr was used as initiator, indicating that the number of active species remained constant during the polymerization. As can be seen in **Figure 2**, the molecular weights of polymers increased with monomer conversion, but were much higher than predicated by calculation(Mn_{th}), and the initiation efficiency($f=Mn_{th}/Mn_{GPC}$) of 2-EBP was higher than that of 1-PEBr. 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, and inefficient initiation that presumably caused by slow deactivation. The polydispersities of polymers remained quite low($Mw/Mn<1.2$) throughout the reaction. **Figure 3** indicated that the specific rotation values of poly((-)-MnMA)s increased slightly with the increase of Mn . The CD spectra(**Figure 4**) are almost independent on Mn , which implies the similar chiral conformation for the menthol unit both in monomer and in polymer. This phenomenon indicates the polymer is not in helical conformation⁴.

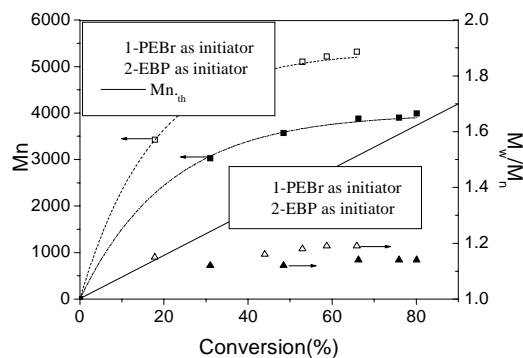
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Figure 1 Kinetic plots for the ATRP of (-)-MnMA using THF as solvent.



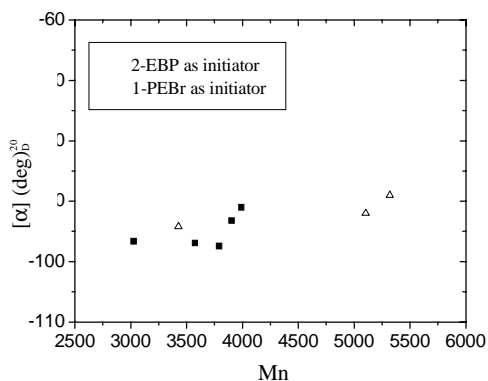
Conditions: 80°C [(-)-MnMA]=0.40M;
[2-EBP]=1/2[CuCl]=1/6 [bpy]= 0.020M;
[1-PEBr]=1/2[CuCl]=1/6 [bpy] = 0.020M.)

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



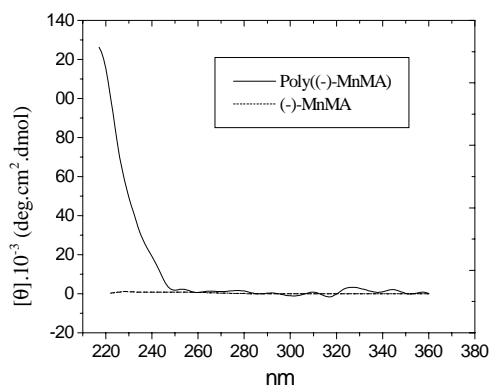
See Figure 1 for conditions.

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



See Figure 1 for conditions.

Figure 4 CD spectra of Poly((-)-MnMA) ($Mn_{GPC}=3960$, $Mw/Mn=1.14$) and (-)-MnMA in CH_2Cl_2 at room temperature.



References

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