

Copolymerization of Styrene with N-phenylmaleimide by Rare Earth Coordination Catalysts

Yan Bing LU, Wei Lin SUN, Zhi Quan SHEN*

Institute of Polymer Science, Zhejiang University, Hangzhou 310027

Abstract: Copolymerization of styrene (St) with N-phenylmaleimide (NPMI) was studied with rare earth coordination catalyst $\text{Nd}(\text{naph})_3\text{-AlEt}_3$ in toluene. Characterization of the copolymers showed that the copolymers possess an alternating structure.

Keywords: Copolymerization, styrene, N-phenylmaleimide, rare earth coordination catalyst.

Copolymers involving NPMI have stimulated great interests because the incorporation of NPMI units into thermoplastic resins may greatly improve the heat-resistance and chemical stability of the products. Free radical copolymerizations of styrene with N-phenylmaleimide have been reported in many papers¹⁻⁴, and the copolymerization is dominated by alternating copolymerization with the participation of monomer charge transfer complex (CTC) in both initiation and chain propagation. Shen *et al.* reported the copolymerization of styrene with maleic anhydride by rare earth coordination catalysts⁵. This paper reports the copolymerization of styrene with N-phenylmaleimide with rare earth coordination catalyst $\text{Nd}(\text{naph})_3\text{-AlEt}_3$ in toluene at 50°C.

St and NPMI can not homopolymerize using the rare earth catalyst $\text{Nd}(\text{naph})_3\text{-AlEt}_3$ in toluene. But copolymers are obtained when St and NPMI are added into the catalyst together. The compositions of St-NPMI copolymer with various monomer feeds are listed in **Table 1**. It showed that the copolymers possess a predominantly alternating structure in a large range of the monomer feeds.

Table 1 Composition of St-NPMI copolymer^a

| | NPMI in monomer (mol%) | Yield(%) | Nitrogen content(%) ^b | NPMI in copolymer (mol%) ^c |
|---|---------------------------|----------|-------------------------------------|--|
| 1 | 10 | 22.27 | 4.30 | 40.6 |
| 2 | 20 | 39.30 | 4.58 | 44.0 |
| 3 | 40 | 58.25 | 4.74 | 46.0 |
| 4 | 50 | 55.93 | 4.79 | 46.7 |
| 5 | 60 | 52.57 | 4.93 | 48.5 |
| 6 | 80 | 30.28 | 5.36 | 54.2 |
| 7 | 90 | 14.87 | 5.71 | 59.2 |

a $[\text{Nd}(\text{naph})_3]=5.0 \times 10^{-3}$ mol/L, $[\text{AlEt}_3]=4.5 \times 10^{-2}$ mol/L, $[\text{St}]+[\text{NPMI}]=8.0 \times 10^{-3}$ mol/L, temperature:50°C, time: 6 h, solvent: toluene; b Measured by elemental analysis;

c Calculated based on the nitrogen content from the elemental analysis

From the ^{13}C NMR spectrum of the copolymer **4** (**Figure 1**), the peak at $\delta = 138.40$ ppm is assigned to the NPMI-St-NPMI triad⁶, and the bands of NPMI-St-St + St-St-NPMI and St-St-St triads do not appear. Conclusion can be drawn that the copolymer **4** is alternating, which is coincident with **Table 1**.

The copolymers exhibit a single glass transition temperature T_g at 227°C (**Figure 2**), reflecting their relatively homogeneous molecular structure. The high T_g of the copolymer results from the five-member planar ring of the imide residues, hindering the rotation around the backbone chain of the macromolecules.

Figure 1 ^{13}C NMR spectrum of copolymer **4** in CDCl_3

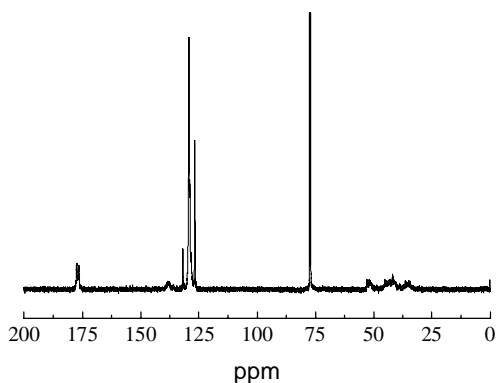
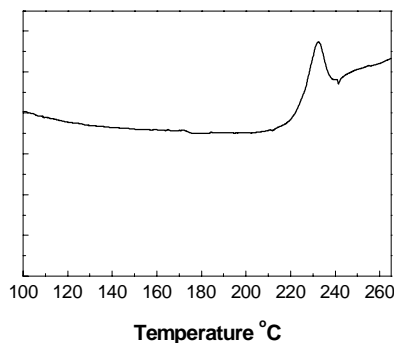


Figure 2 DSC of the copolymer **4** at a heating rate of $10^\circ\text{C}/\text{minute}$



Conclusion

Copolymers of styrene and N-phenylmaleimide are obtained using rare earth coordination catalyst $\text{Nd}(\text{naph})_3\text{-AlEt}_3$. The copolymers obtained are predominantly alternating in structure clarified by elemental analysis and ^{13}C NMR.

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