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Introduction

Crosslinked polymers or polymer networks, are an important class of polymers. Due to the insolubility of polymer network, it is a challenge to characterize the structure of the complicated macromolecular structure.

We propose the synthesis of decrosslinkable polystyrene network with cleavable and uniformly distributed branch units via radical coupling polymerization. This new polymerization system allows us to explore the nonlinear polymerization process by direct experimental methods.

Results and Discussion

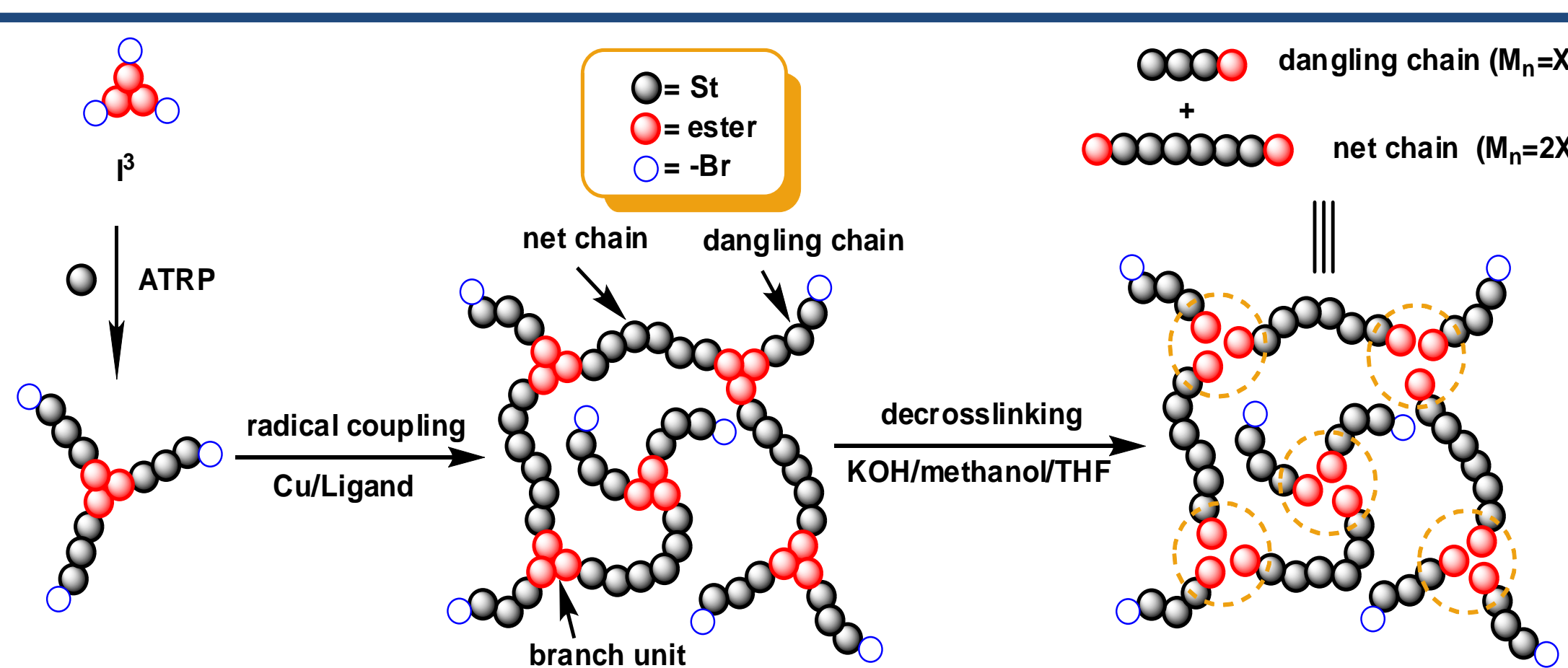


Table 1. Kinetics study of 3-arm polystyrene^a

Run	Time (min)	p_{sol}	W_{sol} (%)	p_{gel}	W_{gel} (%)	p_{total}
1	30	0.07	100	-	-	0.07
2	85	0.178	100	-	-	0.178
3	120	0.329	100	-	-	0.329
4	125	0.334	100	-	-	0.334
5	130	0.417	100	-	-	0.417
6	140	0.460	100	-	-	0.460
7	153	0.503	7.69	0.703	91.1	0.687
8	158	0.571	5.74	0.714	93.2	0.706
9	163	0.575	3.88	0.734	94.6	0.728
10	217	-	trace	0.767	96.7	0.767
11	268	-	trace	0.772	96.9	0.772
12	337	-	trace	0.776	95.8	0.776

^a General conditions: [TPS]:[Cu]:[TPMA] = 1: 3: 3, [TPS] = 0.02 M, THF, 40 °C.

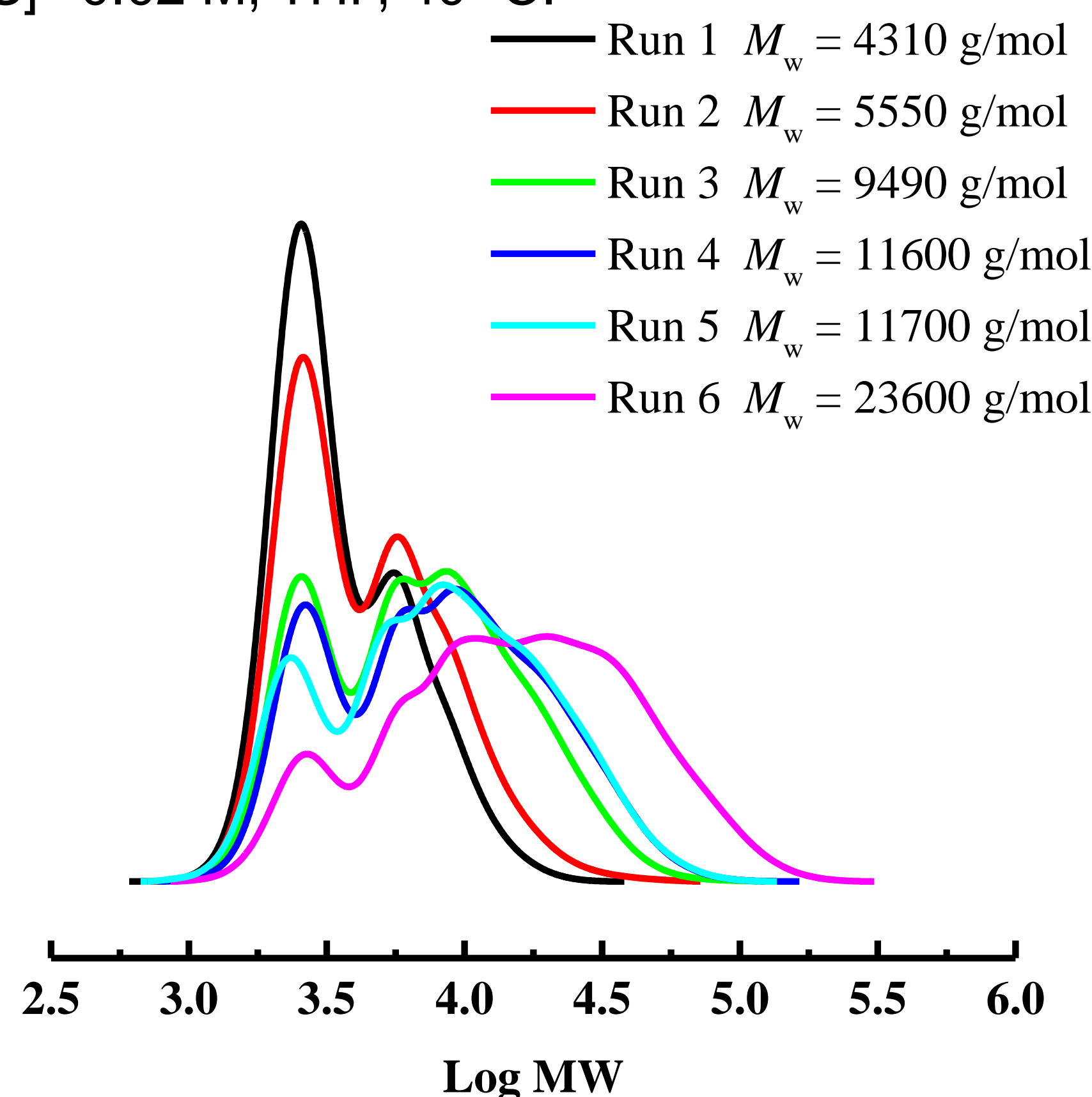


Figure 1. GPC curves of Run 1 to Run 6.

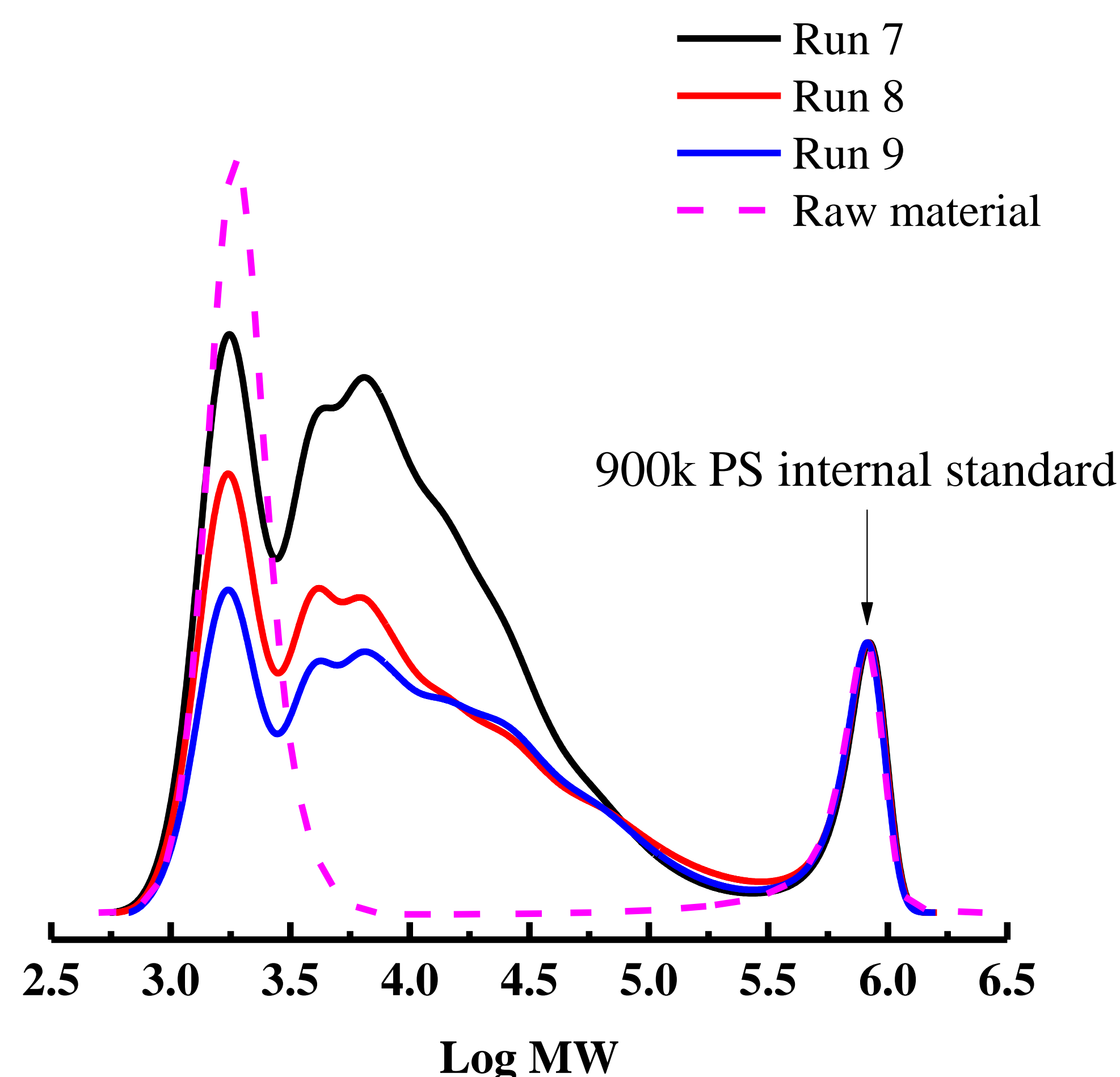


Figure 2. GPC curves of the sol part of Run 7 to Run 9 and raw material against 900 kg/mol PS internal standard for calibration.

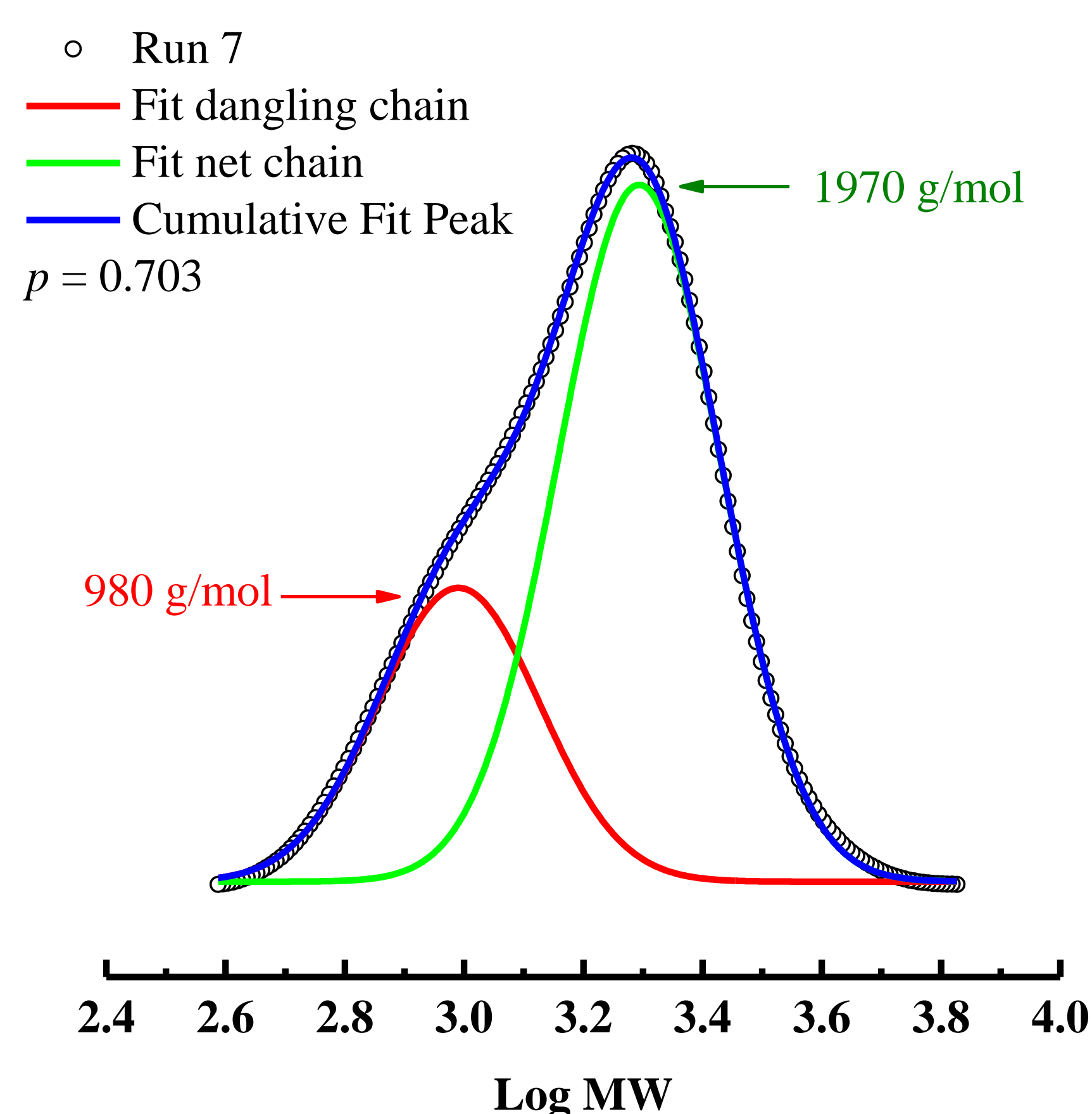


Figure 3. Peak fitting results of alcoholized sample Run 7, $p = S_{net} / (S_{dangling} + S_{net})$.

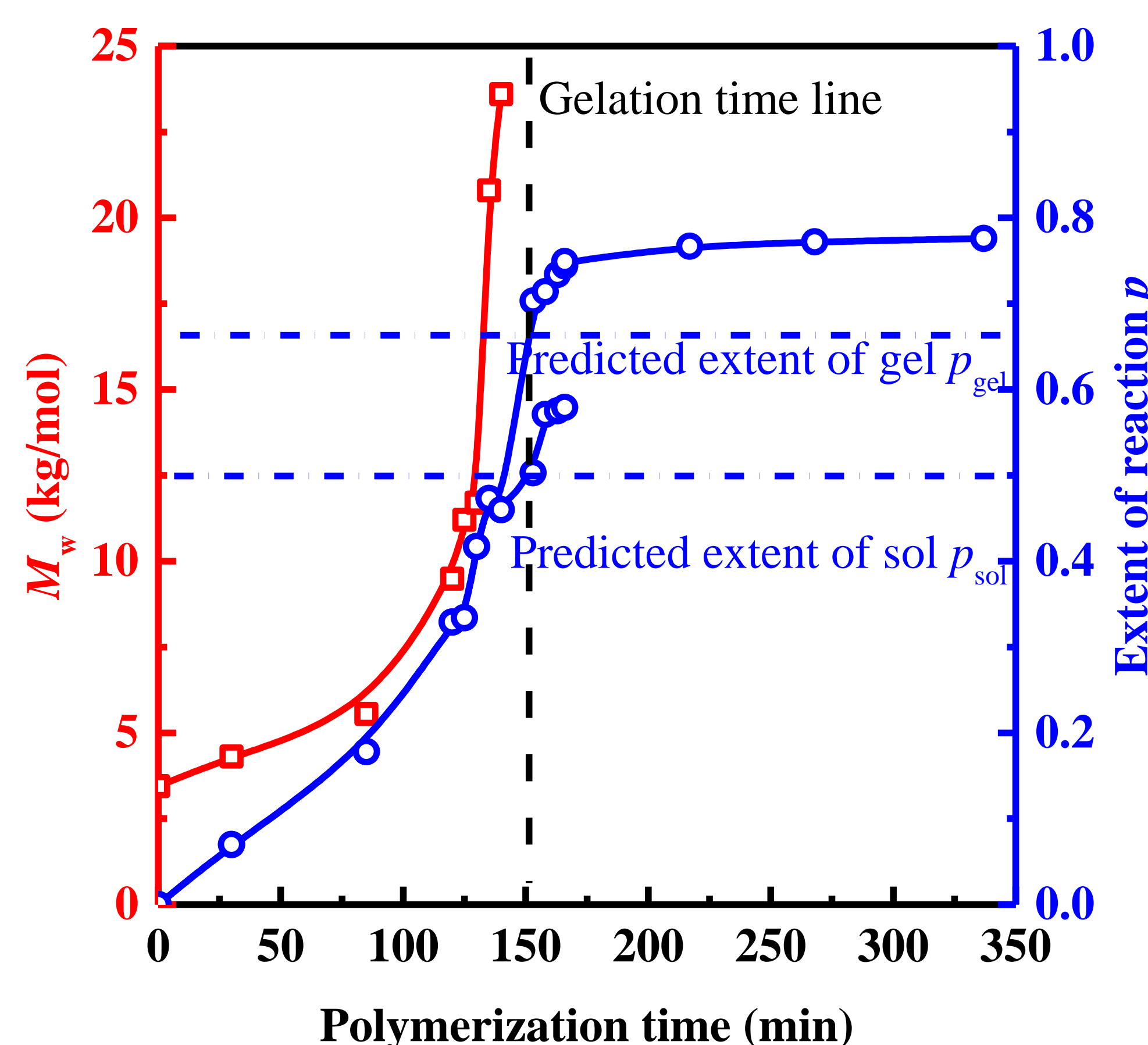


Figure 4. Variation of weight-average molecular weight (M_w) and the extent of reactions (p) with polymerization time.

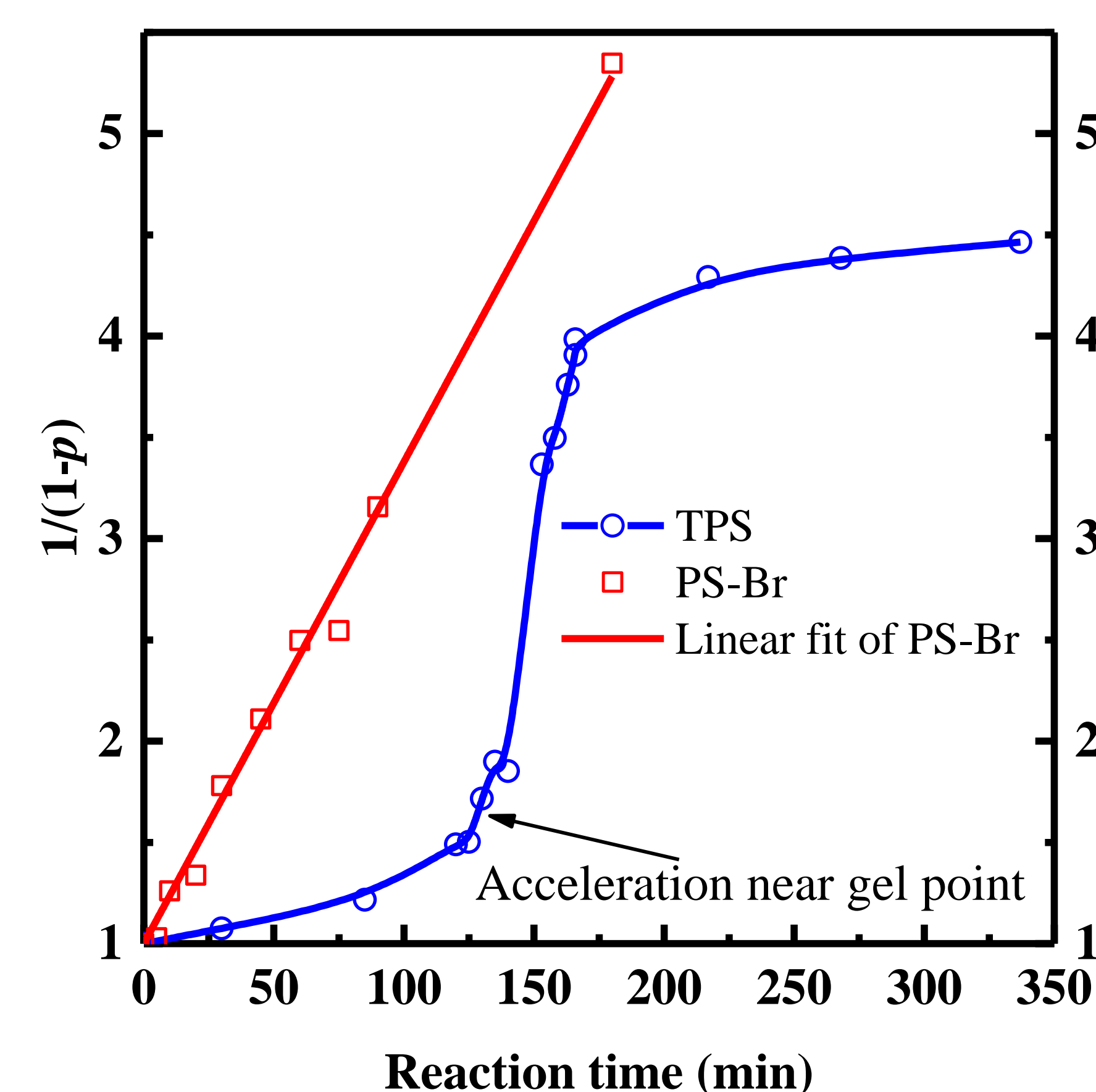


Figure 5. Comparison of the kinetics of coupling reaction of 3-arm polystyrene to linear PS-Br.

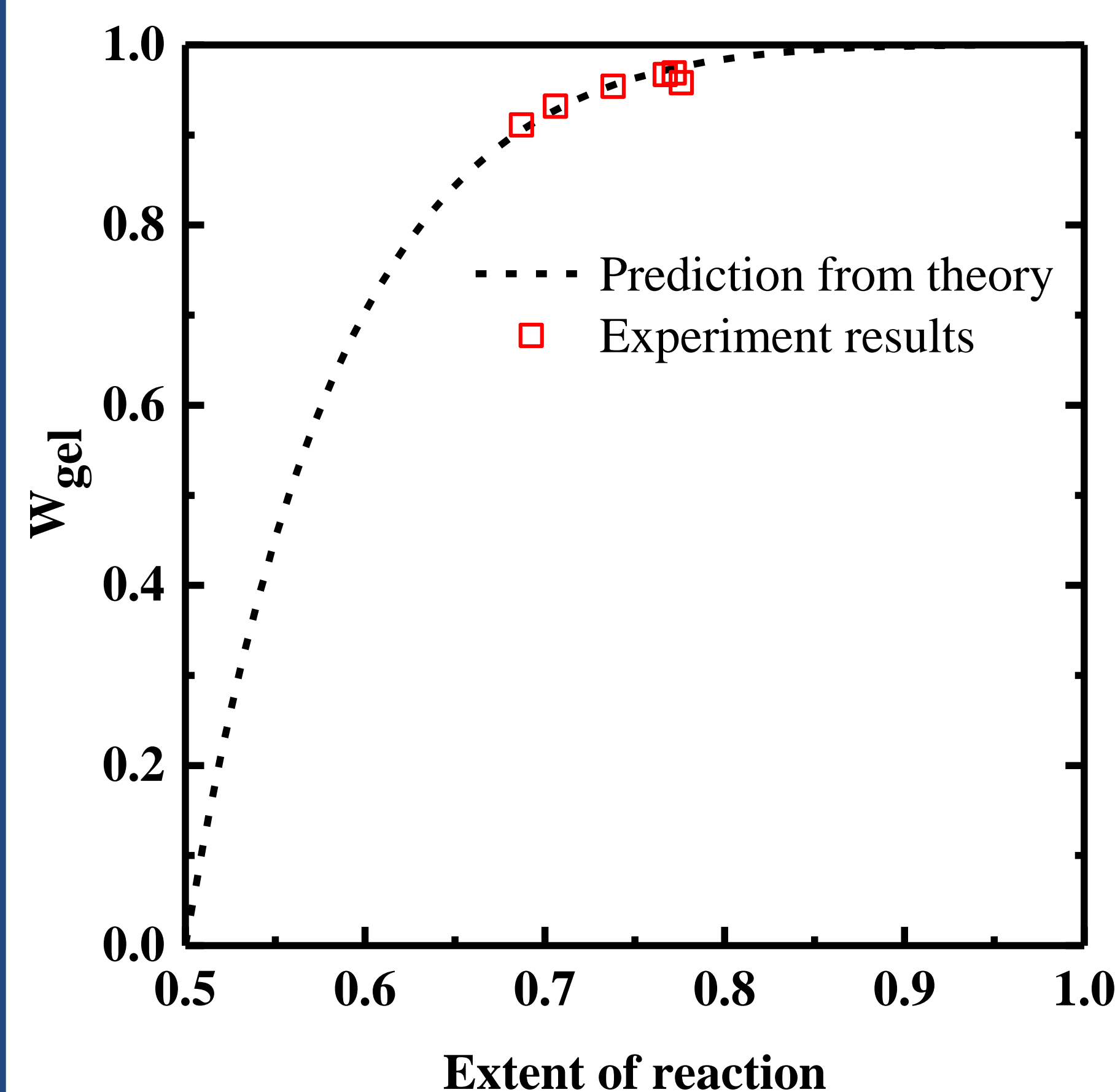


Figure 6. Variation of gel fraction (W_{gel}) with the extent of reaction (p_{total}) after gelation.

Conclusion

We demonstrate the synthesis of decrosslinkable polystyrene network with uniform distribution of branch unit which cannot be prepared by conventional polycondensation or addition polymerization. This two-step method has following advantages.

- (1) The crosslinked polymer with cleavable branch unit allows to obtain p for sol, gel and the whole by GPC measurement after decrosslinking.
- (2) The structure of polymer network can be reconstructed based on cleaved product.
- (3) The 3-arm precursor is prepared by ATRP and the molecular weight of its arm can be tailored and the molecular weight distribution is narrow. This allows us to prepared CPS with different crosslinking density and almost uniform distribution of branch point.

Financial support from National Natural Science Foundation of China (112301-N11222).

References: (1) Odian, G., Principles of Polymerization. Fourth Edition ed.; Wiley & Sons, Inc.: Hoboken, New Jersey, 2004; (2) Flory, P. J.; Rehner, J. J. Chem. Phys. 1943, 11(11), 521-526; (3) Musto, P.; Ragosta, G.; Abbate, M.; Scarinzi, G. Macromolecules 2008, 41(15), 5729-5743; (4) Jean, Y. C.; Deng, Q.; Nguyen, T. T. Macromolecules 1995, 28(26), 8840-8844; (5) Sagidullin, A. I.; Furo, I. Langmuir 2008, 24(9), 4470-4472; (6) Baba, M.; Nedelec, J. M.; Lacoste, J.; Gardette, J. L.; Morel, M. Polym. Degrad. Stabil. 2003, 80(2), 305-313.