

Research on Polymer Modifiers of Bio-asphalt Synthesized by Controlled/Living Radical Polymerization

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Abstract. Bio-asphalt is a new material compared with petroleum asphalt. The bio-asphalt is prepared by bio-oil, which is produced by fast pyrolysis of biomass. Disadvantages of bio-oil are instability and poor high and low temperature performance. Considering these shortcomings, a polymer modifier with controlled number-average molar mass and well-defined microstructure was prepared by controlled/living radical polymerization. In this research, the modifier was added in bio-asphalt to prove its performances which were evaluated by three major indexes tests of asphalt. Test result shows that the modified bio-asphalt has good stability and good high and low temperature performance. In conclusion, the polymer modifiers, synthesized by controlled/living radical polymerization, have excellent modification effect on bio-asphalt.

1. Introduction

In recent years, the unstable situation of oil resources has been forcing road researchers to keep searching for alternative materials of petroleum asphalt binders [1]. Therefore, it has become a hot spot in the field of pavement engineering to research and develop new material to replace petroleum asphalt [2]. As a new type of asphalt material, bio-asphalt has been paid more and more attention by researchers. It is extremely urgent to study the production, performance improvement and pavement use of bio-asphalt [3].

In this research, alkenes polymer modifiers were prepared by controlled/living radical polymerization. These modifiers have active groups that can be react with active groups in bio-asphalt. In addition to this, the number-average molar mass M_n of the active groups in the modifiers is in an appropriate range (15000~100000), which is similar with the saturated main chain in conventional asphalt, and this improves compatibility between the bio-oil and the asphalt. Mix the bio-asphalt with different kinds of polymer modifiers to prepare modified bio-asphalt. Conduct consistency test, softening point test and ductility test on the modified bio-asphalt, and then compare the performance of the modified bio-asphalt and conventional asphalt. At last, it was analyzed how the different polymer modifiers affected the bio-asphalt.

2. Experimental Sections

2.1. Design discipline

(1) There are polar groups like cyan groups, ester groups and carbonyl groups in bio-oil. Therefore, polymer modifiers with similar polar groups on the molecular chains are needed to improve stability of bio-asphalt.



(2) Make the number-average molar mass of the polymer modifiers synthesized by controlled/living radical polymerization in an appropriate range (15000~100000). Meanwhile, choose styrene monomers, acrylate monomers and butadiene monomers that all contain active groups to polymerize polymeric substances with active groups.

2.2. Raw material

2.2.1. *Bio-oil*. Bio-oil contains almost all kinds of Oxygen-Bearing Organic Matters like ethers, esters, aldehydes, ketones, organic acids, alcohols and so on. By organic elemental analysis, it is known that the components of the bio-oil are 74.42% of carbon, 13.39% of oxygen, 10.095% of hydrogen, 1.92% of nitrogen and 0.17% of sulphur.

2.2.2. Basis bitumen

In this research, 90# basis bitumen was selected. Table 1 shows its technical indexes.

Table 1. Performance parameters of the 90# basis bitumen

| Entry | Units | Criterion | Testing results |
|----------------------------------|---------|-----------|-----------------|
| Penetration(25°C, 5s, 100g) | [0.1mm] | 60~80 | 62.7 |
| Ductility(5°C, 5cm/min) | [cm] | ≥30 | 43 |
| Softening point | [°C] | ≥42 | 54 |
| Kinematic viscosity(135°C) | [Pa•s] | ≤3.0 | 1.136 |
| Flash point | [°C] | ≥230 | 258 |
| Relative density | [—] | — | 1.015 |
| Quality change | [%] | ≤±0.8 | -0.523 |
| Residual penetration ratio(25°C) | [%] | ≥65 | 78 |
| Residual ductility(10°C,5cm/min) | [cm] | ≥15 | 20 |

2.2.3. *Synthesis of polymer modifiers*. The controlled/living radical polymerization was used to synthesize the polymer modifiers. Normally, there are two methods of the controlled/living radical polymerization, Reversible addition-fragmentation chain transfer (RAFT) polymerization and Degenerative transfer radical polymerization (DTRP) [4-5].

① Synthesis of homopolymer:

The typical RAFT homogeneous polymerization of vinyl monomers is as following: At first, put vinyl monomer, RAFT reagent, initiator (azo) and solvent (benzene) in dry round bottomed flask equipped with a magnetic bar. In this polymerization, the molar concentration ratio of the monomer and the RAFT reagent is 150 – 1000, and the molar concentration ratio of the RAFT reagent and the initiator is 3 – 5. Then remove oxygen in this hierarchy by placing the hierarchy in frozen brine and argon bubbling for 10 minutes. Afterwards, the flask was degassed by five freeze-thaw-pump cycles, kept under argon and placed in an oil bath thermostated at 60°C. At the designed time, add mineral ether in the flask to stop the reaction. Use the polymer obtained for follow-up tests. In the RAFT polymerization, the RAFT reagent has selective regulation on vinyl monomers. For example, ethyl 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (EPDTB) is an effective regulatory agent of styrene(St) and

chloroprene (CP) as well as the 4-cyano-4-(phenylcarbonothioylthio) pentanoic acid (CPDTB) is an effective regulatory agent of methyl methacrylate (MMA).

The typical DTRP homogeneous polymerization of vinyl monomers is similar with RAFT homogeneous polymerization. In DTRP, it is also needed to select appropriate DTRP to regulate a particular monomer. For example, methenyl iodide is an effective regulatory agent of St and St, and the cyanopropyl iodide (CP-I) is an effective regulatory agent of n-Butylacrylate (BA) and MMA.

The polymer modifiers with appropriate structure and formula weight could be synthesized in heterogeneous polymerization by the controlled/living radical polymerization. Chloroprene monomer is a kind of vinyl monomers with high activity. Take the controlled/living radical polymerization of chloroprene monomer in emulsion as an example to demonstrate how to conduct synthesis of polymer modifiers.

Oil phase: Put 34.2g disproportionated rosin, 2.97-5.85g of the RAFT reagent (DBTTC) or degenerative transfer agent (CHI_3) into 900g of chloroprene monomer and dissolve fully. Water phase: Put 6.57g of NaOH, 1.80g of lauryl sodium sulfate, 3.60g of Lomar PW, 1.80g of NaCO_3 into 990g of distilled water and dissolve fully.

Emulsion polymerization: At first, put the prepare water phase into the low temperature emulsion polymerization hierarchy and then stir it. Meanwhile, put the prepared water phase into the hierarchy and purge nitrogen to isolate the hierarchy from the air. Secondly, pre-emulsificate the hierarchy at 20°C for 35 minutes and then cool it down to 10°C and add aqueous solution of $-\text{K}_2\text{S}_2\text{O}_8$ as an oxidant. Next, use peristaltic pump to add prepared deoxidizer, aqueous solution of Na_2SO_3 and thiourea dioxide sodium salt. Keep the temperature of polymerization at 9°C . During polymerization, take a little polymer emulsion and use weighing method to monitor the conversion rate of the chloroprene monomer. After the polymerization finished, put the emulsion into a large amount of methanol to gel precipitated. After desiccation, use the product to conduct follow up tests like GPC, ^1H NMR.

② Synthesis of block copolymer:

The idea of using RAFT to synthesize polymeric modifiers is shown in figure 1 as following. Firstly, use the method of synthesis of homopolymer mentioned above to synthesize macromolecule RAFT reagent. Then, add in monomer B, conduct polymerization and obtain block copolymer modifiers.

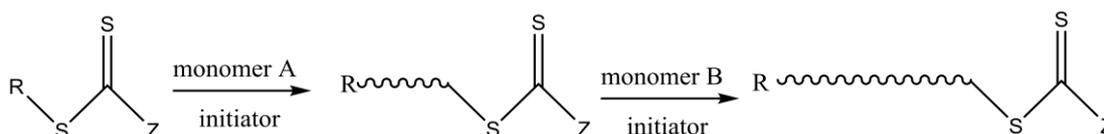


Figure 1. Add monomers in series to synthesize AB diblock copolymers.

Take PSt-*b*-PCP and PMMA-*b*-PCP as examples to demonstrate the detailed process of the synthesis.

Synthesis of PSt-*b*-PCP: According to synthesis of homopolymer, synthesize the RAFT reagent, Pst. Wash the methanol gel precipitation for three times and obtain PSt ($M_n = 2900 \text{ g mol}^{-1}$, $M_w/M_n = 1.23$), and then use PSt as the RAFT reagent to conduct the block polymerization of chloroprene. The prescription is PSt (2g), chloroprene monomer (20.21g, 138mmol), initiator AIBN (0.0283g, 0.17mmol) solvent benzene (30.3g). Use the product to conduct follow up tests.

Synthesis of PMMA-*b*-PCP: Similar as above, synthesize the RAFT reagent, PMMA ($M_n = 1800 \text{ g mol}^{-1}$, $M_w/M_n = 1.33$). Then use PMMA as the RAFT reagent to conduct the block polymerization of chloroprene. The prescription is PMMA (2g, 1.11mmol), chloroprene monomer (25g, 113mmol), initiator AIBN (0.0096g, 0.588mmol) and solvent benzene (30g). Use the product to conduct follow up tests.

The idea of using DTRP to synthesize polymeric modifiers is as following. Firstly, synthesize polymer DTRP agent. Then, add in monomer B, conduct polymerization and obtain block copolymers modifiers. This process is similar with the synthesis process of PSt-*b*-PCP and PMMA-*b*-PCP as mentioned above.

③ Synthesis of bio-asphalt

First, add the polymer modifiers into bio-oil as designed dosage and keep the temperature at 165°C. Melt the basis bitumen and add in the modified bio-oil and use high speed shearing emulsifying machine shear the mixture at 3000r/min for 10 minutes, then the modified bio-asphalt is obtained.

④ Three indicators of asphalt

Penetration is the viscosity index of asphalt, which reflects the softness of asphalt under certain conditions and temperatures. The smaller the penetration, the harder the asphalt. The softening point is the temperature when the asphalt meets the required viscosity. The higher the softening point, the higher the stiffness modulus of the same condition. The emulsification point can be used as the evaluation index of high temperature stability. Low temperature ductility is an important index for evaluating the cracking resistance of asphalt. When the temperature drops, due to the deformation ability of the asphalt chemical composition, the dislocations and sliding ability of the molecules, the decrease of asphalt ductility is very significant.

3. Testing results analysis

3.1. Synthesis of polymer modifiers

It is obtained that the number-average molecular weight M_n of the polymer modifiers produced by the controlled/living radical polymerization is 30900. Its polydispersity index of molecular weight M_w/M_n is narrower (2.22) than the polymer produced by normal radical polymerization. This indicates that its microstructure is clear, see in figure 2.

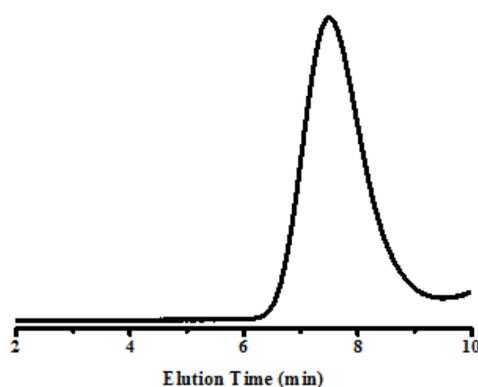


Figure 2. Typical GPC curve graph of polymer modifier synthesized by controlled/living radical polymerization ($M_n = 30900$, $M_w/M_n = 2.22$).

Figures 3, 4 and 5 are nuclear magnetic hydrogen spectra of photopolymers synthesized by controlled/living radical polymerization. From these figures, it can be observed distinct characteristic peaks of the monomers and molecular weight regulators. This indicates that the reactions have been conducted according to the mechanism of controlled/living radical polymerization.

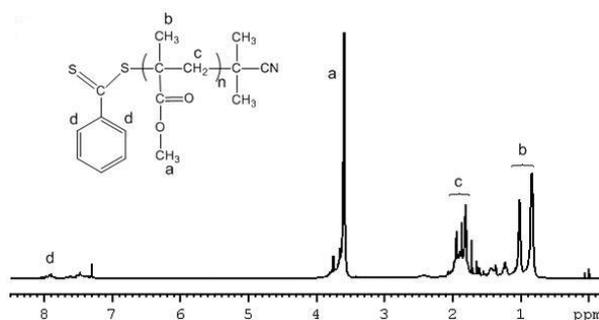


Figure 3. Nuclear magnetic hydrogen spectrum of PMMA synthesized under regulation with CPDB as RAFT reagent.

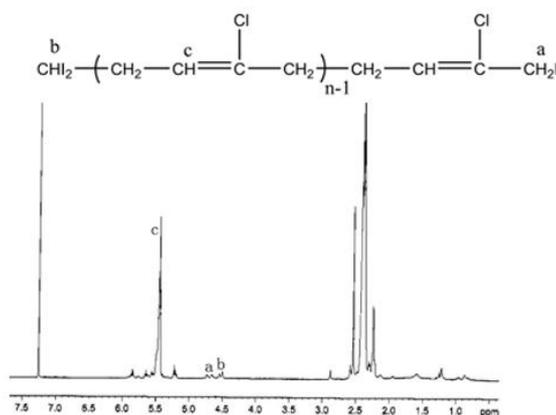


Figure 4. Nuclear magnetic hydrogen spectrum of PCP synthesized with methenyl iodide as DTRP agent.

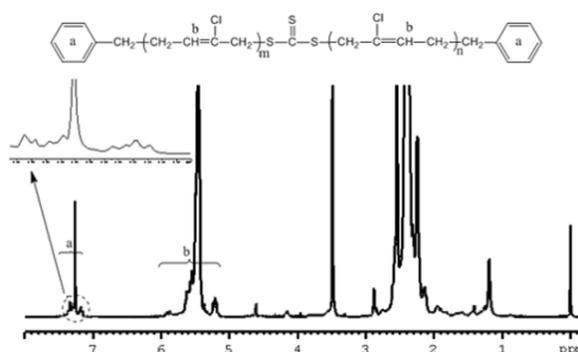


Figure 5. Nuclear magnetic hydrogen spectrum of PCP synthesized by chloroprene emulsion polymerization with DBTTC as RAFT reagent.

Conduct $^1\text{H-NMR}$ on RAFT synthesized block copolymer. As shown in figure 6, the ^1H NMR spectrum indicates that the characteristic peaks of chemical shift at 6.3-7.2ppm and 5.2-5.9ppm respectively belongs to polystyrene and the methyldyne protons of RAFT end group. This proves that the structure of PSt-*b*-PCP is diblock polymers. Considering the controlled radical polymerization, the synthesized block copolymer is PSt-*b*-PCP.

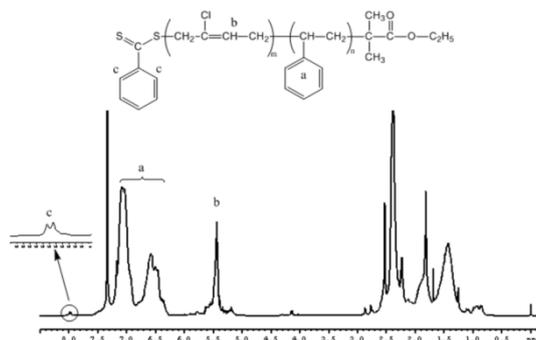


Figure 6. Nuclear magnetic hydrogen spectrum of PSt-*b*-PCP.

Conduct $^1\text{H-NMR}$ on DTRP synthesized block copolymer. As shown in figure 7, the ^1H NMR spectrum indicates that the a peak at 5.1-5.9 ppm chemical shift belongs to the characteristic peak of the methyldyne on main chain of polychloroprene. The b peak at 3.6 ppm is the characteristic peak of the methyl protons of PMMA. The c peak at 2.9 ppm is the characteristic peak of the β -end methylene

protons adjacent to iodine of chain end. This testing result further proved PCP-*b*-PMMA was successfully synthesized [7].

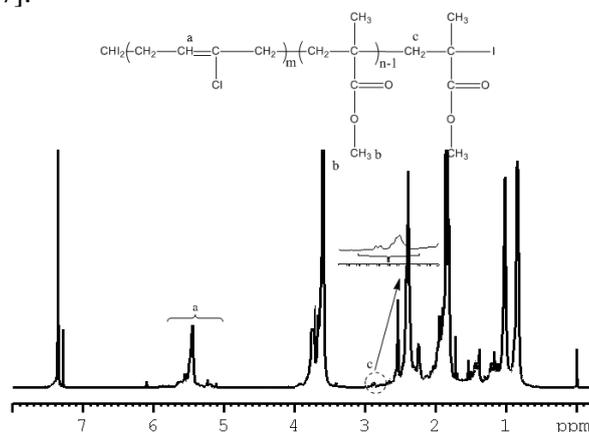


Figure 7. Nuclear magnetic hydrogen spectrum of PCP-*b*-PMMA.

Based on the analysis above, the designed polymer modifiers are successfully synthesized by controlled/living radical polymerization.

3.2. The three indexes of bio-asphalt

Conduct the tests of the three index of asphalt on the modified bio-asphalt, and the testing results is shown in table 2.

Table 2. The three indexes of bio-asphalts.

| Modifiers | Three indexes | | |
|---------------------------------------|----------------------------|-------------------------|-------------------------|
| | Penetration [25°C, dmm] | Softening point [°C] | Ductility [10°C, cm] |
| PMMA(CPDTB) | 64 | 50 | 47.6 |
| PCP(CHI ₃) | 71 | 43 | 51 . 2 |
| PCP(DBTTC) | 68 | 44 | 50.5 |
| PMMA- <i>b</i> -PCP(CPDB) | 67 | 46 | 49.2 |
| PCP- <i>b</i> -PSt(CHI ₃) | 65 | 49 | 49 |

From table 2, it can be told that the three index of the modified bio-asphalt are excellent so the bio-asphalt has good high and low temperature performance. The reason why the modified bio-asphalt has good performance is as following. Firstly, the synthesized polymers have appropriate number-average molecular weight (15000-100000) which is similar with the basis bitumen. Secondly the monomers chosen to be synthesized are styrene monomers, acrylate monomers and butadienes monomers so that the synthesized modifiers have active groups that can react with the active groups of the bio-asphalt. This increases the stability of the bio-asphalt. Meanwhile, the modifiers and the basis bitumen have similar saturated main chains that makes they are compatible to each other. On the other hand, traditional modifiers of asphalt always have huge number-average molecular weight which is way higher than 100,000. In addition to this, their main chains are saturated alkanes. Therefore, the way they modifying the bio-asphalt is just physical blending but on chemical reaction that leads to poor compatibility of polymer modifiers and bio-asphalt.

From table 2, there are two laws for the penetration and the ductility of the modified bio-asphalts. For the penetrations, $PCP(CHI_3) > PCP(DBTTC) > PMMA-b-PCP(CPDB) > PCP-b-PSt(CHI_3) > PMMA(CPDTB)$; for the ductilities, $PMMA(CPDTB) > PCP-b-PSt(CHI_3) > PMMA-b-PCP(CPDB) > PCP(DBTTC) > PCP(CHI_3)$. The reason for this phenomenon is that PMMA has the highest rigidity of main chain; PSt takes second place and PCP is less than both of the formers.

4. Summary

(1) Use controlled/living radical polymerization method to polymerize the alkene monomers (styrene monomers, acrylate monomers and butadienes monomers) to synthesize modifiers for bio-asphalt. The testing results of the gel permeation chromatography indicate the number-average molecular weights of the modifiers are in an appropriate range (15,000-100,000). The nuclear magnetic hydrogen spectra indicate the modifiers are homopolymers or two block copolymers with clear structure. All these mean that it is successfully synthesized designed modifiers.

(2) Use the synthesized modifiers to modify the bio-asphalt. Testing results show that the modified bio-asphalt is stable and has good performances.

5. References

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