Polymer 55 (2014) 4468–4477

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Effect of chain length distribution on thermal characteristics of model polytetrahydrofuran (PTHF) networks

Ruilan Guo [a], Karl I. Jacob [b, c, *]

[a] Department of Chemical and Biomolecular Engineering, University of Notre Dame, South Bend, IN 46556, USA
[b] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0295, USA
[c] G.W.Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0295, USA

ARTICLE INFO

Article history:
Received 2 April 2014
Received in revised form
27 May 2014
Accepted 8 June 2014
Available online 13 June 2014

Keywords:
Polytetrahydrofuran
Networks
Unimodal

ABSTRACT

A series of model polytetrahydrofuran (PTHF) networks were synthesized via end-linking reactions of α, ω-allyl PTHF oligomers with a stoichiometric tetrafunctional crosslinker. The telechelic PTHF oligomers were synthesized by living cationic ring-opening polymerization of tetrahydrofuran followed by a termination reaction with allyl alcohol. Networks thus prepared have well-controlled architecture in terms of the inter-crosslink chain length (M_c) and chain length distribution: resulting in unimodal, bimodal and clustered structures. Unimodal network was prepared by using polymer chains of same molecular weight, bimodal networks were synthesized by using two groups of polymer chains with different average molecular weights, and the clusters are prepared by incorporating clusters of networks with small molecular weight chains in a network matrix made of longer chains. Thermal characteristics of these model networks were investigated as a function of crosslink density, as well as inhomogeneities of crosslink distribution using DSC. We demonstrate that glass transition temperature (T_g) and crystallization behavior (melting temperature and crystallinity) of the networks are both strongly influenced by crosslink density (M_c). By comparing the unimodal, bimodal and clustered networks with similar average M_c, the effects of inhomogeneities in the crosslink distribution on the thermal properties were also investigated. Results show that inhomogeneities have trivial influence on T_g, but strongly affects the crystallization behavior. Moreover, the effects of the content ratio and length ratio between long and short chains, and the effects of cluster size and size distribution on the thermal characteristics were also studied.

1. Introduction

Effect of molecular level structure on the physical, morphological and conformational properties (such as deformation behavior, crystallization, developmental segmental orientation, etc.) of polymer materials has long been a field of major interest. It is of particular interest and importance to control the molecular architecture of crosslinked polymers to study the resulting behavior, i.e., inhomogeneities or heterogeneities in crosslinks, which have significant practical relevance in determining their macroscopic properties [1,2]. Inhomogeneities in a polymer network or gel in principle leads to inhomogeneous responses from the network reflecting in their macroscopic properties, such as turbidity of gels [3–5], swelling and shrinking [6,7], rheology properties [8,9], mechanical properties [10–13], and so forth. Polymer networks are normally prepared through random crosslinking processes, like vulcanization using sulfur, peroxide thermolysis, and radiation, generally with polymer chains with a broad distribution of molecular weight. In such polymer networks, the presence of defects, such as differential chain lengths and the presence of pendent chains, loops, double connections and trapped entanglements, cannot be avoided, which makes the structure of networks too complicated to be characterized at the molecular level. Therefore, in order to better understand the physical principles involved in the behavior of elastomers and to verify the limitations of existing rubber elasticity theories for such networks, it would be ideal to synthesize the so called “model” or “ideal” networks with well-defined chain length and chain length distribution between crosslinks via controllable crosslinking process, such as end-linking of telechelic curable oligomers. A significant advantage of the end-

---

* Corresponding author. School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0295, USA. Tel.: +1 404 894 2541; fax: +1 404 894 9766.
E-mail addresses: karl.jacob@mse.gatech.edu, karl.jacob@ptfe.gatech.edu (K.I. Jacob).

http://dx.doi.org/10.1016/j.polymer.2014.06.026
0032-3861/© 2014 Elsevier Ltd. All rights reserved.

linking approach is that it enables one to prepare networks with rather precisely controlled distribution of chain lengths between crosslinks and provides a beneficial control over defects causing structural components. The most studied model polymer networks are bimodal networks, where two sets of chemically identical telechelic polymer chains of different molar mass are chemically end-linked, resulting in a bimodal distribution in the chain length (M_c) between crosslinks. By purposely introducing crosslinking inhomogeneities into polymer networks, a number of researchers have directed their effort to explore the relationship between the molecular level inhomogeneities and the macroscopic properties of polymer networks, via both experimental and computational modeling approaches. For example, early studies by Mark et al. pointed out that bimodal networks with similar average M_c as that of unimodal networks (one narrow distribution in M_c) have significantly higher ultimate properties possibly due to limited extensibility of short chains [12,13]. However, it is still difficult to express quantitatively the heterogeneity of such a bimodal network structure, e.g. the average size and distribution of small mesh domains, and the average distance between domains, and to explain the ultimate properties as a function of the degree of heterogeneity. Thus many questions concerning the behavior of elastic chains in polymer networks remain open and are still subject to further investigation. Furthermore, clustered networks, where highly crosslinked short chain clusters are chemically embedded in a crosslinked long chain matrix, are new and unique in this study; very limited information is available in the literature on elastomers with well-defined clustered topology. The clustered feature adds a new inhomogeneity level in addition to inter-crosslink chain length (M_c) in polymer networks that may influence the macroscopic properties. It is expected that the difference in the regions of densely crosslinked chains (clusters) and the regions with lower crosslink density should be reflected in the macroscopic properties like thermal characteristics.

In this study, we study the thermal characteristics of model PTHF networks with unimodal, bimodal and clustered distribution of chain length between crosslinks in a systematic fashion. Careful controlled chemistry has allowed us to create a series of model networks with well-defined crosslink density (M_c) and inhomogeneity level, as well as high gel factions. The dependence of thermal characteristics, such as glass transition temperature, melting temperature, and crystallization behavior, has been comprehensively studied in this work.

2. Experimental

2.1. Synthesis and characterization of telechelic PTHF precursors

Mono-dispersed α, ω-allyl polytetrahydrofuran (PTHF) precursors were synthesized through cationic ring-opening polymerization mechanism using trifluoromethanesulfonic anhydride as initiator and allyl alcohol as end-capping agent. Well-controlled molecular weights of telechelic oligomers were feasibly achieved via controlling polymerization temperature and time. A detailed description of synthesis procedures and characterizations can be found in Refs. [14,15] Chemical structure of telechelic oligomers and the completeness of end-capping reaction were confirmed by ^{1}H NMR, FTIR and Raman spectroscopy. Molecular weights of the oligomers were determined using several independent techniques including titration (end-group analysis), ^{1}H NMR (end group analysis) and MALDI mass spectroscopy to ensure its accuracy. Size-exclusion chromatography (SEC) was employed to determine the relative molecular weights and polydispersity using toluene as a mobile phase at 30 °C [15].

2.2. Preparation of model PTHF networks

Model networks were prepared by crosslinking, or more precisely, end-linking diallyl PTHF oligomers using a tetrafunctional crosslinker, *i.e.*, pentaerythritol tetrakis 3-mercaptopropionate (PTMP) [14,16]. The thiol–ene reaction was thermally initiated in solution with a stoichiometric amount of PTMP. The pre-cure reaction was allowed to proceed for 20–30 min to ensure that at least one end of precursors is connected to the crosslinker. This is necessary to prevent phase separation between crosslinker and oligomers after the evacuation of solvent. The pre-reacted solution was then poured into a flat glass mold, which was placed in a vacuum oven at 85 °C. Solvent was quickly removed via N_2 purge and simultaneous vacuum pumping. The final cure process was carried out at 85 °C under N_2 for 48 h to afford networks with high gel fraction.

Unimodal networks were prepared via end-linking one set of oligomers with narrow distributed molecular weight. Bimodal networks were prepared via end-linking two sets of oligomers of different molecular weights, particularly, one set of short chains and one set of long chains. Specially, networks with uniquely clustered structure were prepared following a two-step process: firstly, the end-linking reaction was conducted using very short chains to form the multifunctional “clusters” of high crosslink density, where the size of the clusters was controlled by reactant concentration, stoichiometric ratio and reaction time, or “clustering” time; a set of long chains was then added after certain “clustering” time to continue the end-linking and final curing process. This process results in a “clustered” network structure with highly crosslinked clusters that are chemically embedded in a matrix with long chains.

2.3. Characterization of thermal properties

DSC measurements were carried out on a Seiko Instrument Model DMS210 with liquid nitrogen cooling system (LNCS). All oligomers and networks were completely dried before measurement. A consistent thermal history was ensured for each sample by applying exactly the same heating-cooling conditions. In all measurements, a constant heating rate of 10 °C/min was applied in a temperature range from -120 °C to 90 °C with N_2 purge. Samples were first brought down to -120 °C followed by two heating-cooling cycles. The thermal properties data are reported based on the second heating-cooling cycle. Glass transition temperature (T_g) was determined via the mid-point temperature method, melting temperature (T_m) was assigned by the peak maximum temperature of the melting peak, and enthalpy of fusion (ΔH) was determined from the peak integration of the melting peak using a straight linear baseline. Thermal characteristics were comprehensively investigated as a function of crosslink density (M_c) and inhomogeneities associated with crosslink distribution.

3. Results & discussions

3.1. Synthesis of telechelic PTHF oligomers and model PTHF networks

Telechelic PTHF oligomers with narrowly distributed molecular weight were synthesized via cationic ring opening polymerization followed by a termination reaction with allyl alcohol to introduce curable allyl end groups. Molecular weights of the resulting oligomers were controlled via varying reaction temperature, stoichiometric ratio and reaction time. Allyl terminal functionality was confirmed by ^{1}H NMR and FTIR [15]. Multiple techniques were applied to determine the molecular weights of the oligomers, *i.e.*,