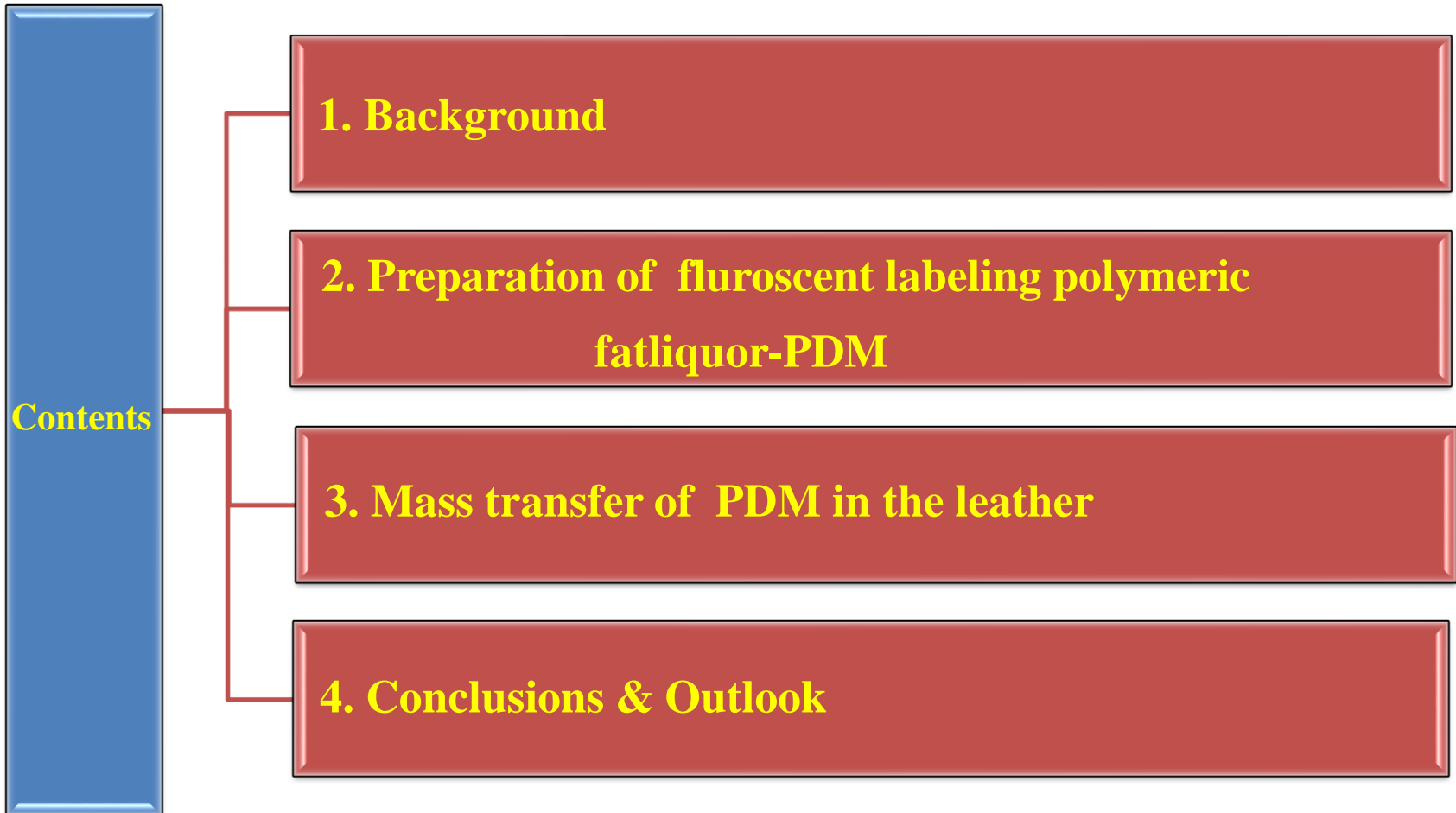


A background image showing a cross-section of leather with a green fluorescent pattern, indicating the distribution of the fluorescent tracer. The pattern is irregular and spread across the surface.

# Fluorescent labeling of polymeric fatliquor and its mass transfer in leather

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19<sup>th</sup> Nov. 2022

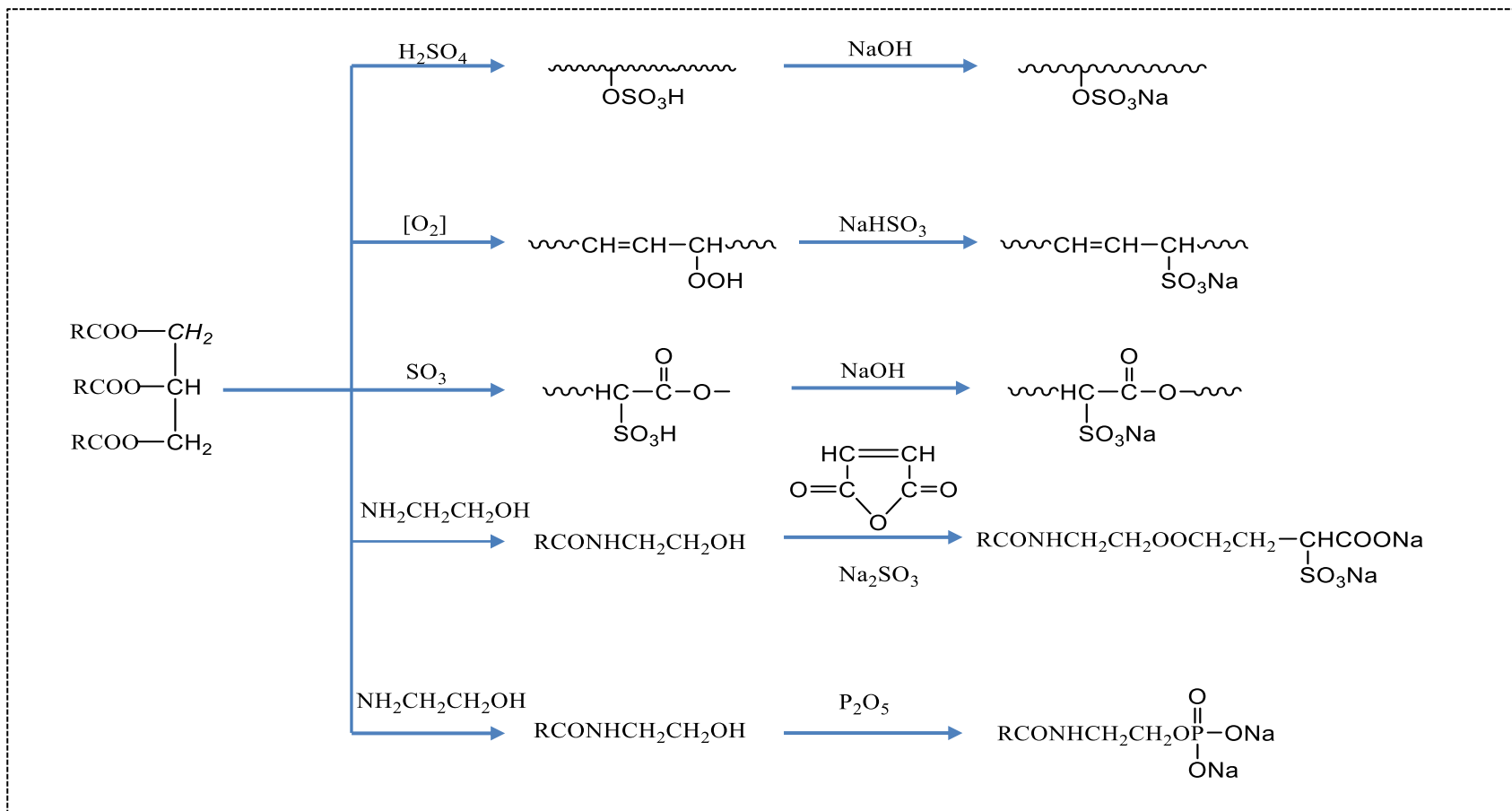


# 1. Background

- Fatliquoring is one of the most important process in leather making.
- Fatliquors are the largest amount of leather chemicals.
  - softness
  - physical and mechanical properties
  - handle
  - water-resistant



## 1.1 The Preparation method of fatliquors



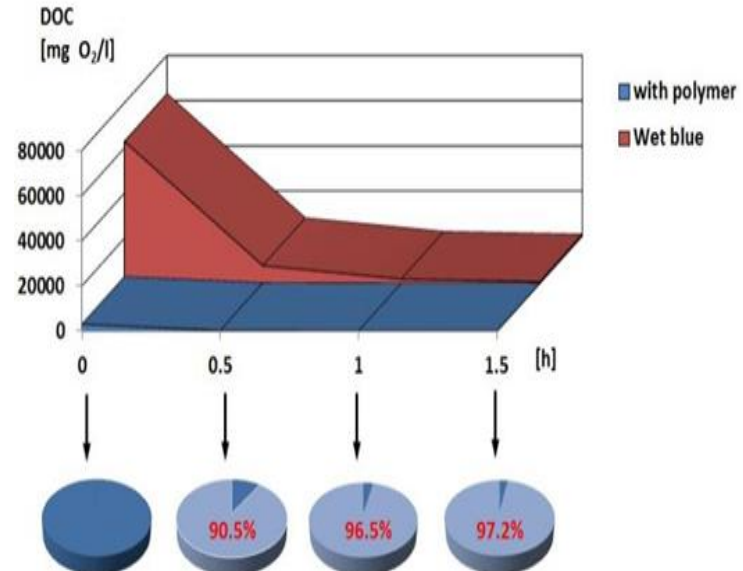
Schematic diagram of preparation routes of conventional fatliquors

## 1.1 The Preparation method of fatliquors

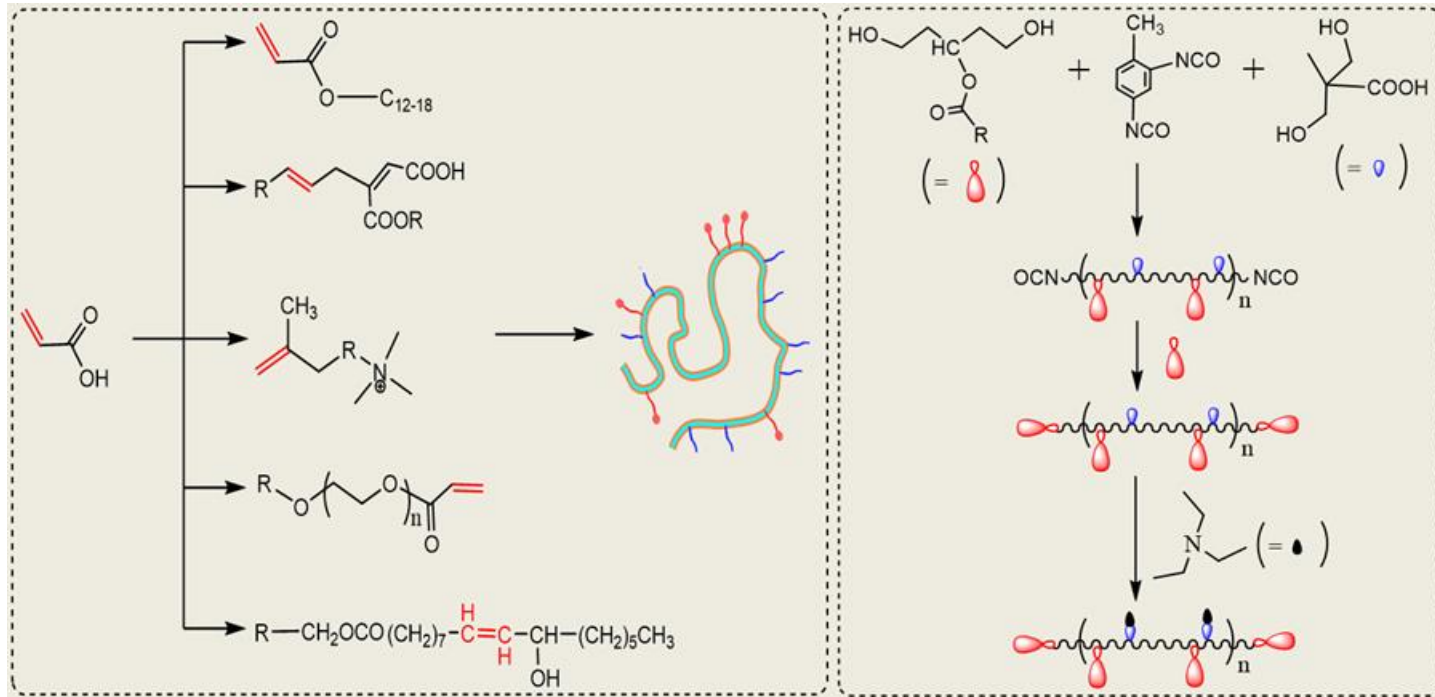
➡ *Polymeric fatliquor has become a new development direction*

The molecular structure of polymer fatliquor contains both long-chain hydrocarbon groups and hydrophilic groups with tanning properties, which play the role of fatliquor, retanning and filling at the same time.

- *softness*
- *lightfast*
- *low fogging*
- *good exhaustion rate*
- *simplification*



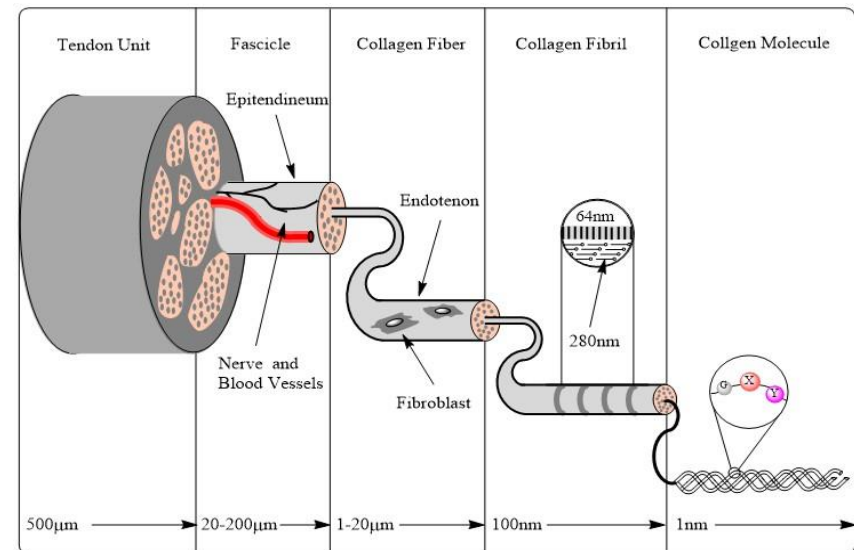
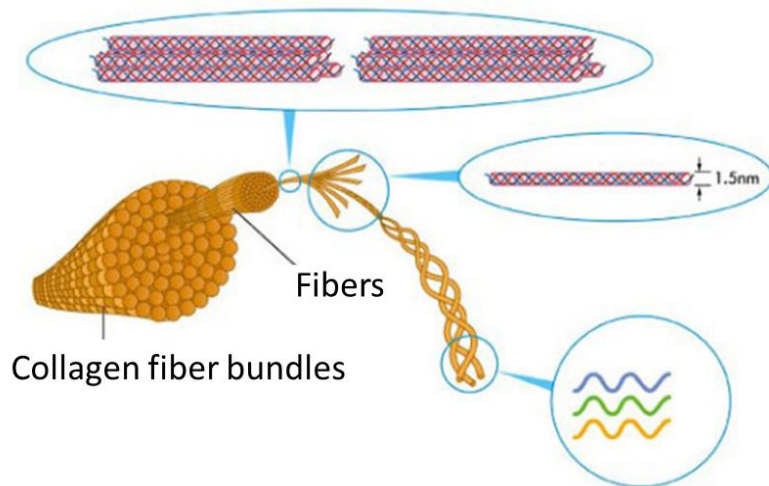
## 1.1 The Preparation method of fatliquors



Schematic diagram of preparation routes of polymeric fatliquor

## 1.2 The penetration and distribution of fatliquors in collagen

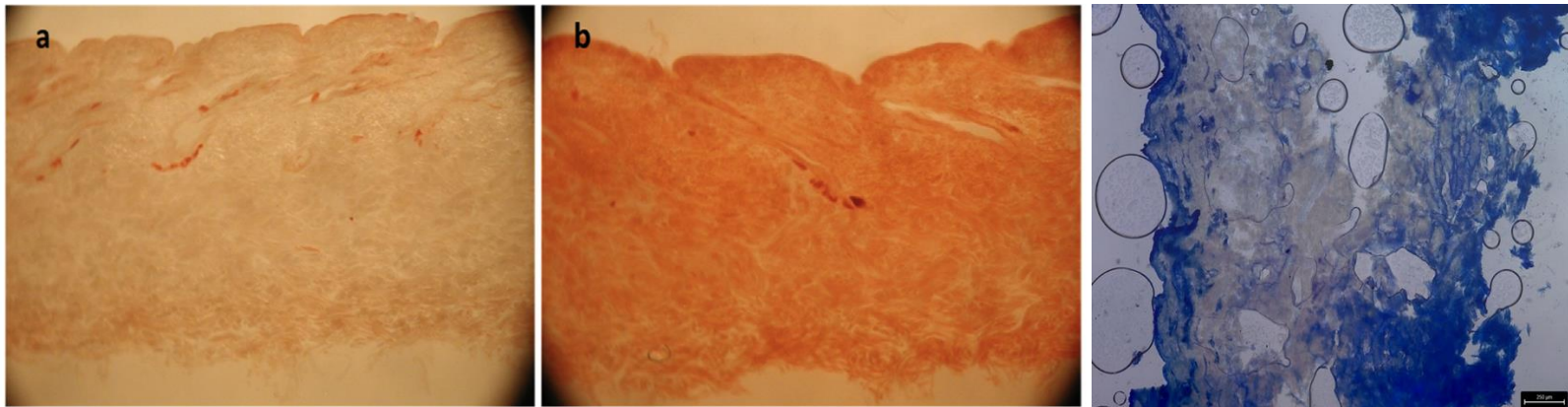
- unique hierarchical structure
  - thickness
  - random weaving state
  - processing mode





## 1.2 The penetration and distribution of fatliquor in collagen

- **Sudan Red IV**
  - the staining rate of Sudan red staining method is low,
  - the discrimination effect is poor.
- **Nerolane sulfate staining**
  - more effective,
  - cannot avoid the interference of the original adipose tissue

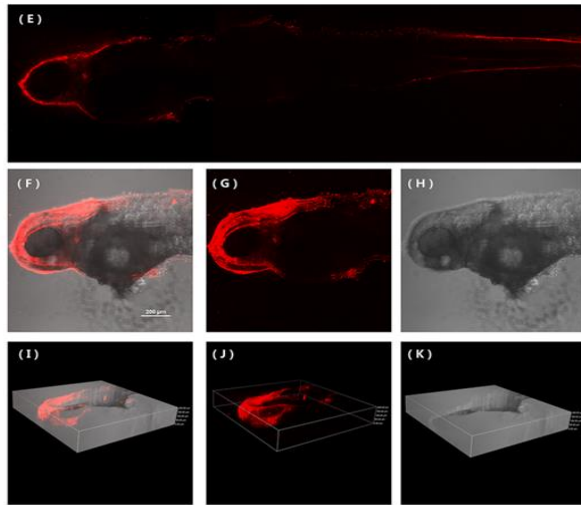


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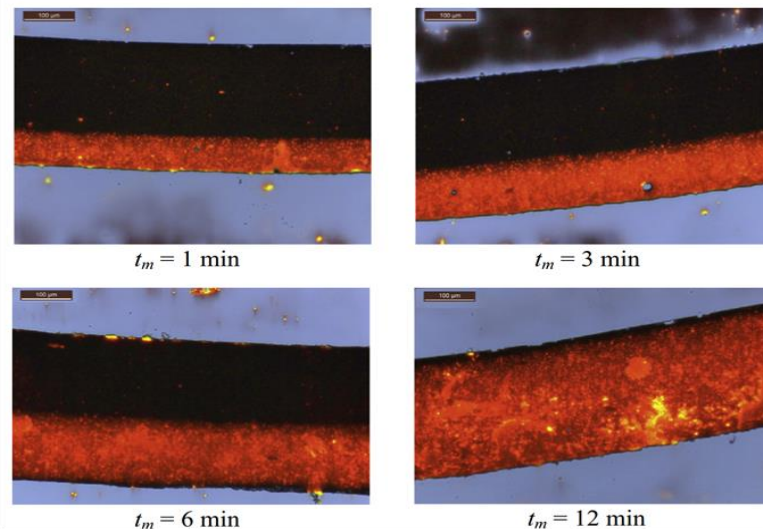


## 1.3 Fluorescence tracer technique

- A sensitive and effective technique
- Can analyze the mass transfer and distribution of chemicals within the leather in real time.

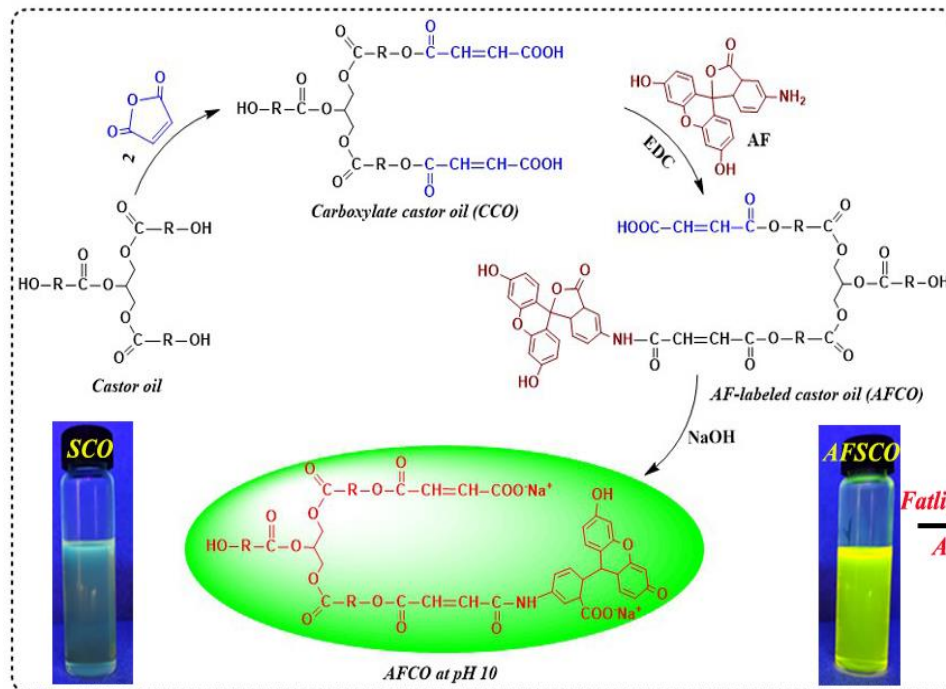


**Dyes and Pigments 191 (2021) 109375**



**European Polymer Journal 66 (2015) 407–418**

## 1.4 Our previous job



*A pH sensitive fluorescent tracer based on castor oil for fatliquor tracing*



*Stained by Sudan IV*



*Stained by Sulphate Nile blue*

*Fatliquored by AFSCO*



*Investigation mass transfer of fatliquor in leather*



*Fluorescent tracing*

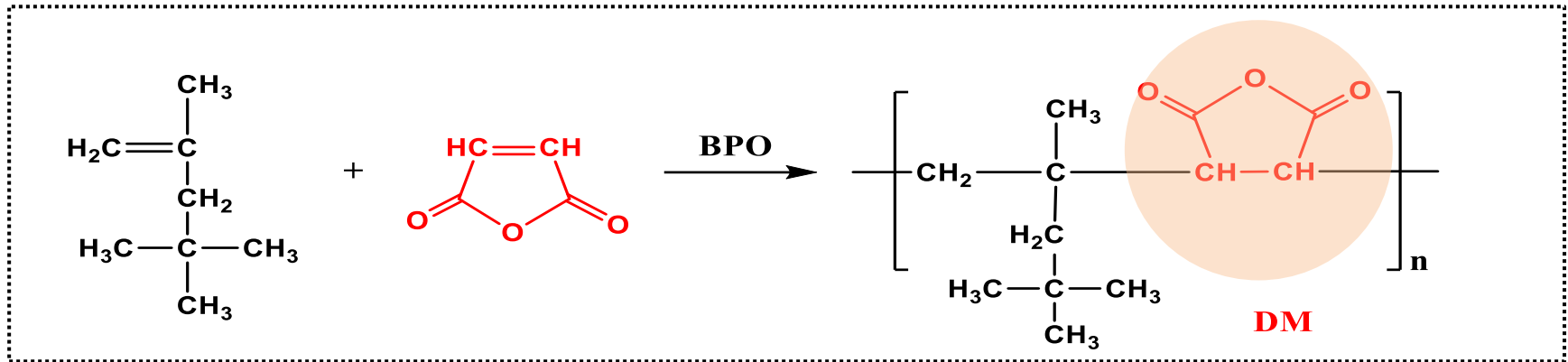
- The fluorescence tracer technique for conventional fatliquors has been preliminarily established.



## 2. The Objectives of this work

- ➔ Construction of a new class of polymer fatliquors based on *poly(diisobutylene-maleic anhydride)* (DM) as a platform
- ➔ The permeation behavior of polymer in leather was studied by labeling the polymer with *5-amino-fluorescein*

## 2.1 Construction of reactive polymer platform



The synthetic principle of ploy(diisobutylene-maleic anhydride)

*Why do we choose it ?*

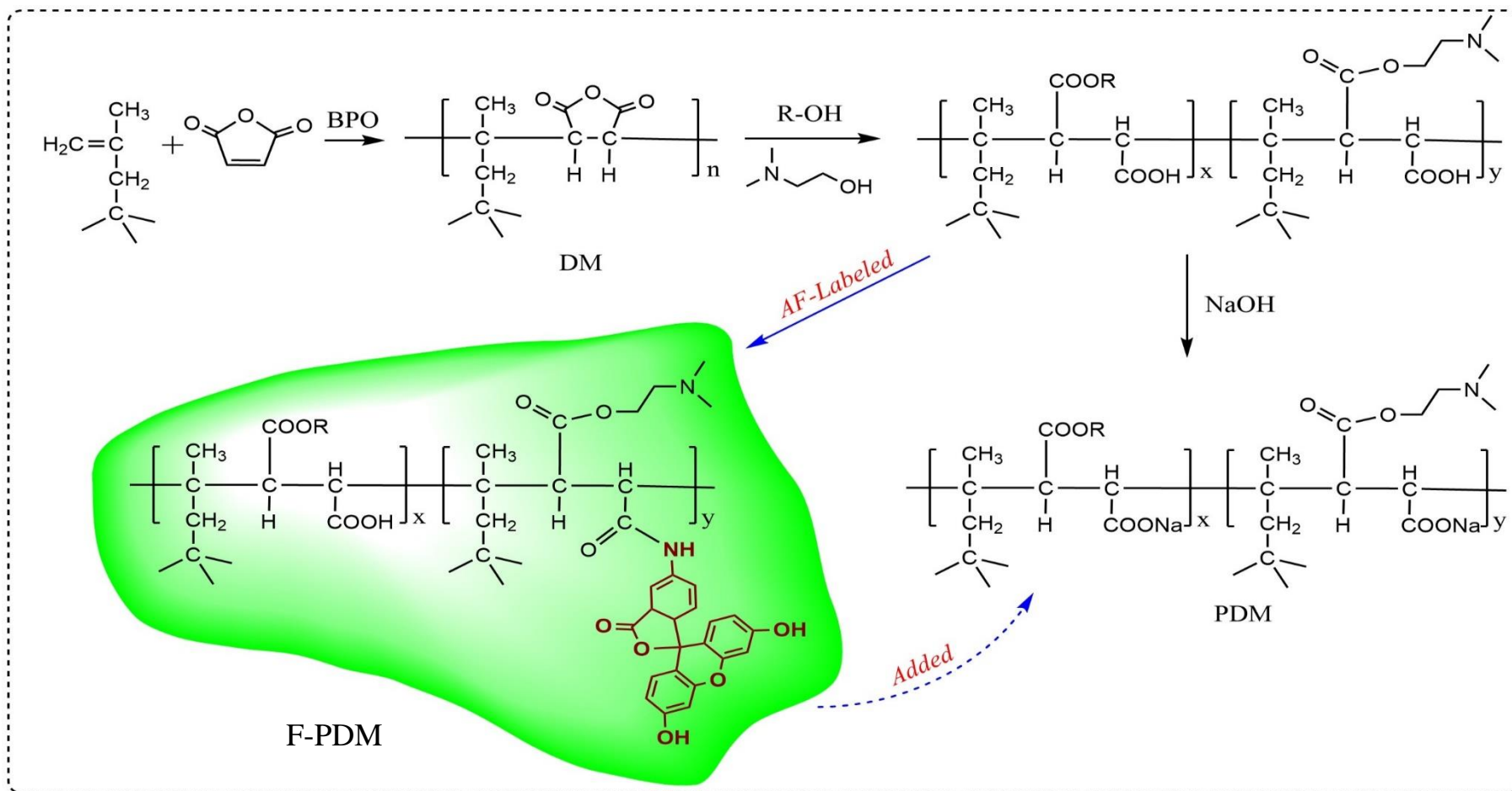
Advantages

sufficient supply in china and not costly

easy to perserve

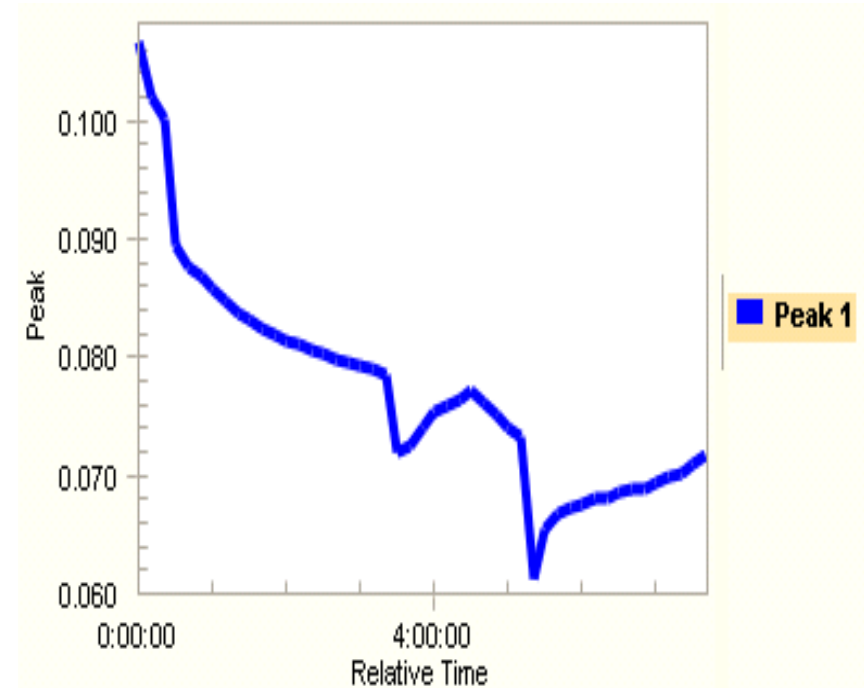
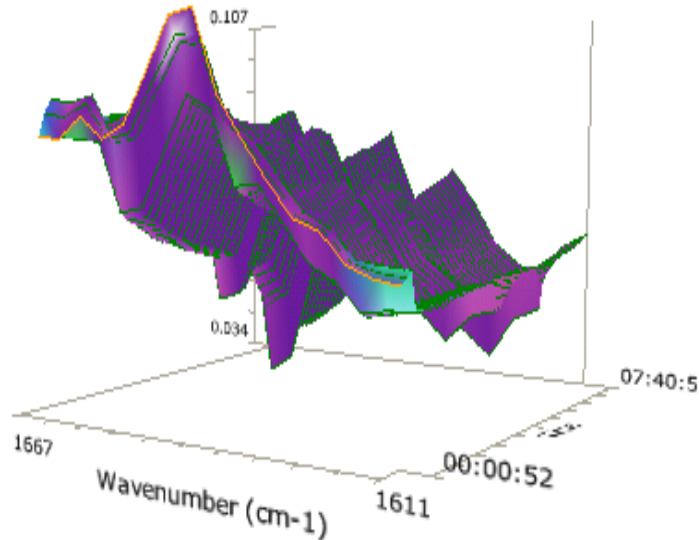
high activity, easy to modify

## 2.2 Preparation route of PDM and F-PDM



The preparation route of PDM and F-PDM

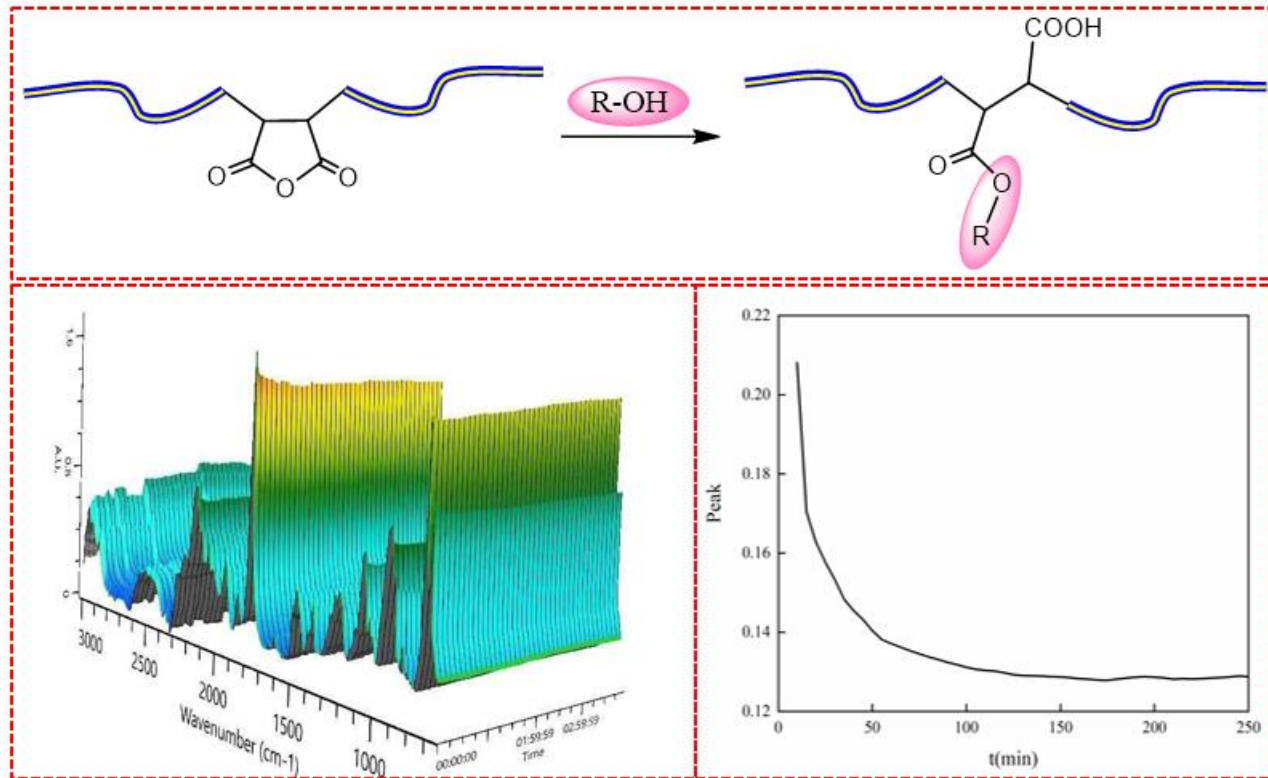
## 2.3 Reaction conditions optimization



- The polymerization was completed in 6 hours.

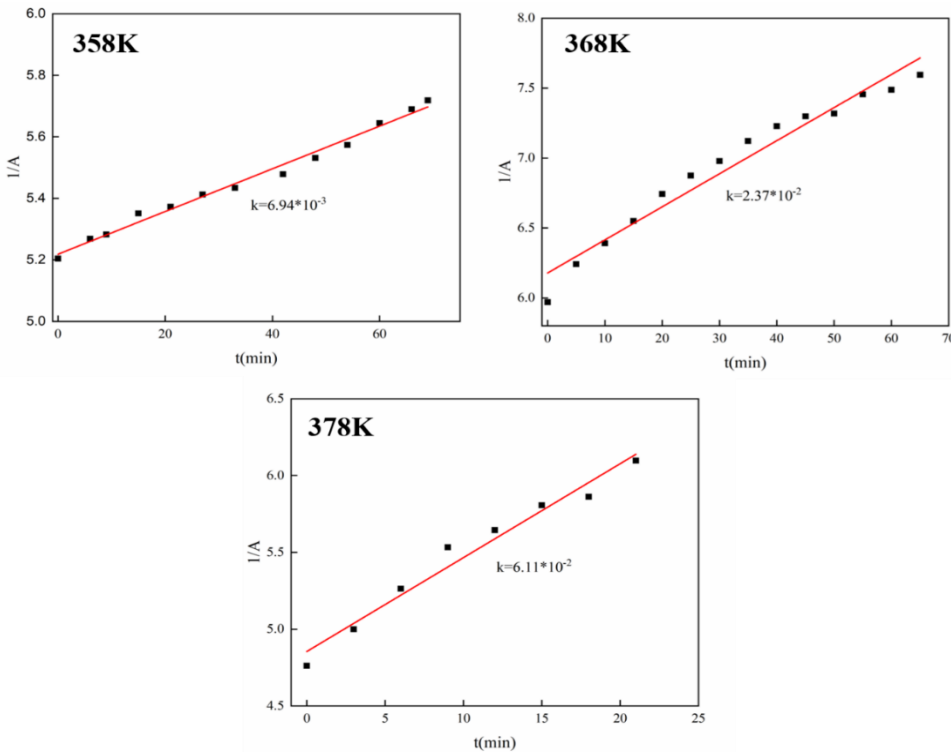


## 2.4 Grafting of polymers with aliphatic alcohols

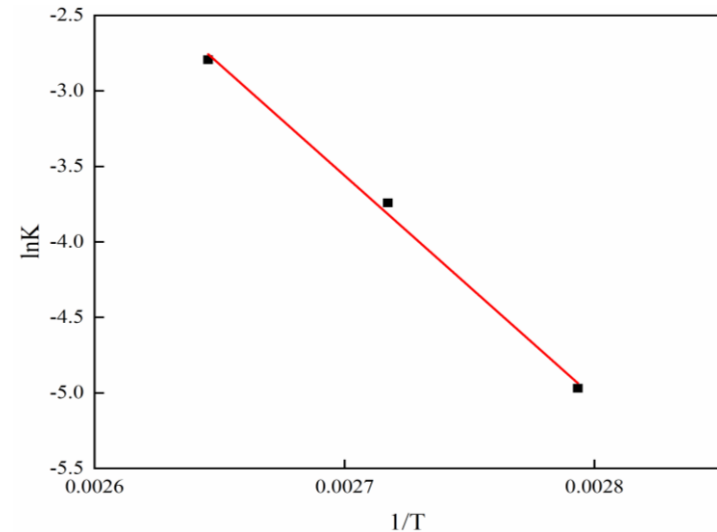


The absorbance of anhydride as a function of time

## 2.5 Grafting of polymers with aliphatic alcohols



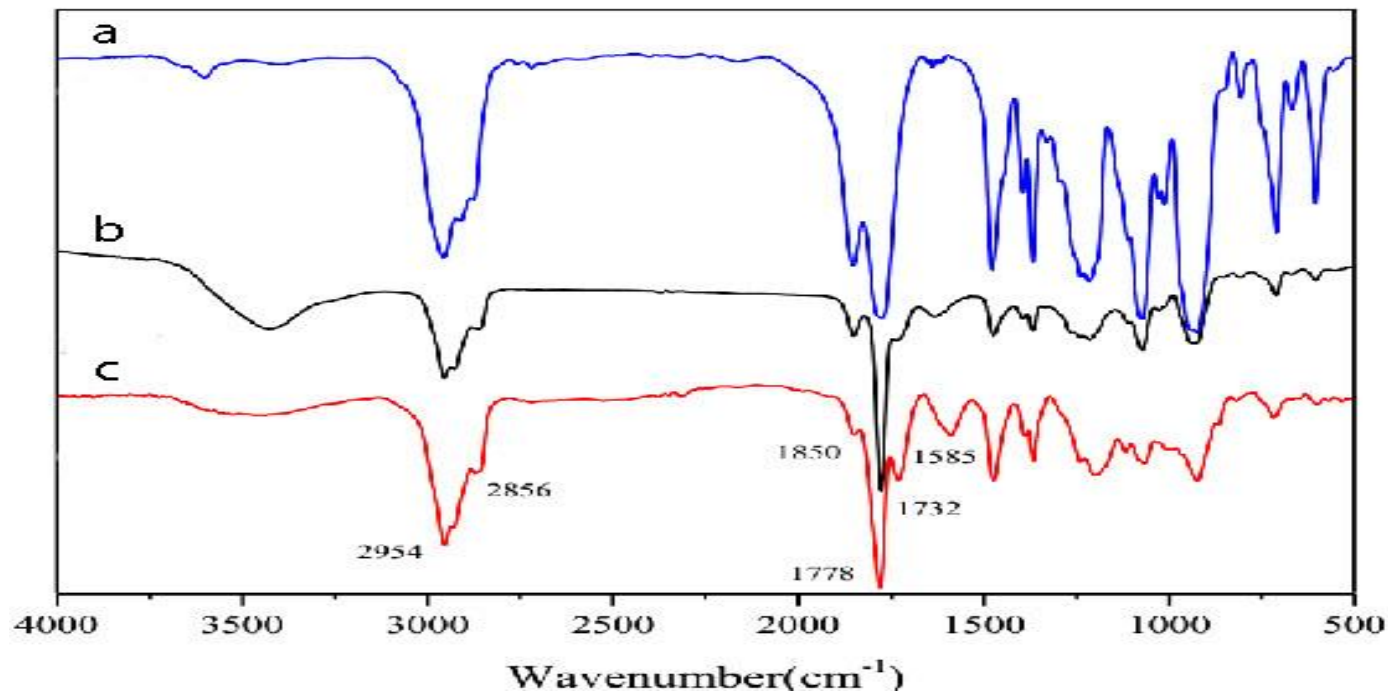
The relationship between the variation of  $1/A$  and time at different temperatures



The reaction activation energy  $E_a$  for the grafting reaction of the system is 14.74 KJ/mol.

## 2.6 Characterization

### a. Infrared spectrum

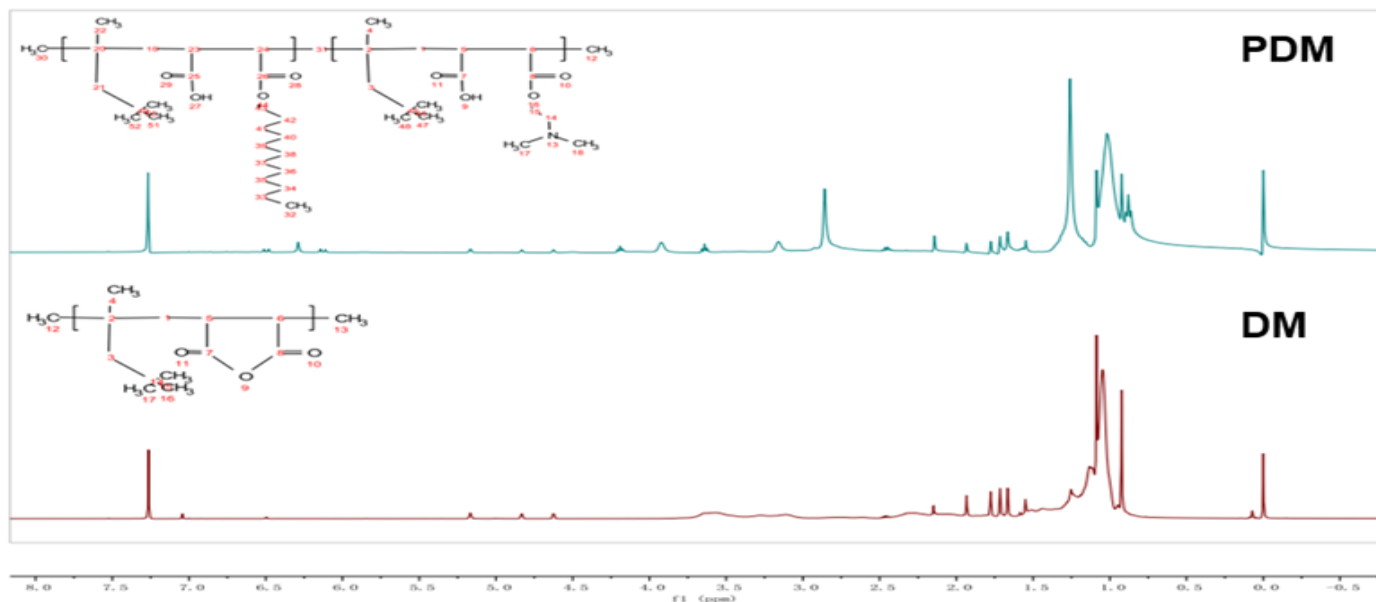


FTIR of DM and PDM

- The absorption peak 1585 cm<sup>-1</sup> (c) is a characteristic absorption peak of the stretching vibration of -C-N, indicating the involvement of DMEM in the esterification reaction.

## 2.6 Characterization

### b. $^1\text{H-NMR}$



the  $^1\text{H-NMR}$  of DM and PDM

- The new chemical shifts ( $\delta=0.85$  and  $\delta=1.24$ ) appear for the terminal methyl group and  $-(\text{CH}_2)_{10}-$  in the dodecanol structure, respectively



## 2.6 Characterization

### *c. GPC*

**Relationship between molecular mass of DM and initiator dosage**

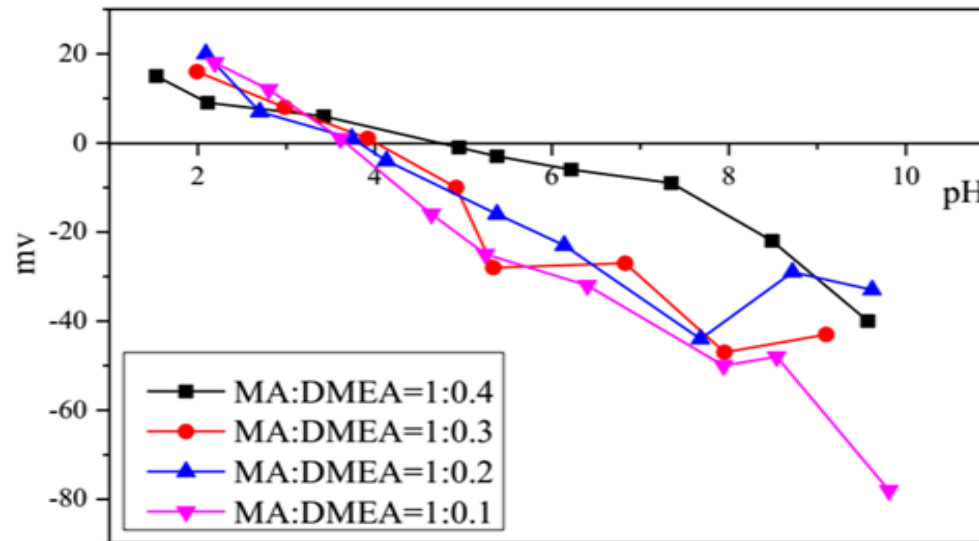
Sample	Initiator(%)	The value of bromine(%)	Mn	Mw	Mz	D
DM--1	1.0	1.28	9658	15890	25760	1.65
DM-2	1.5	1.02	7609	12759	20875	1.68
DM-3	2.0	0.70	6746	11497	19588	1.70

□ The larger the amount of initiator, the smaller the molecular weight



## 2.6 Characterization

### d. Isoelectric point



Effect of DMEA on isoelectric point of polymer fatliquor

- Exhibiting an amphoteric property.
- with the increase of N, N-dimethylethanolamine content, the isoelectric point of polymer fatliquoring increase.



## 2.7 The application of PDM

**The effect of the dosage of grafting agent on PDM properties**

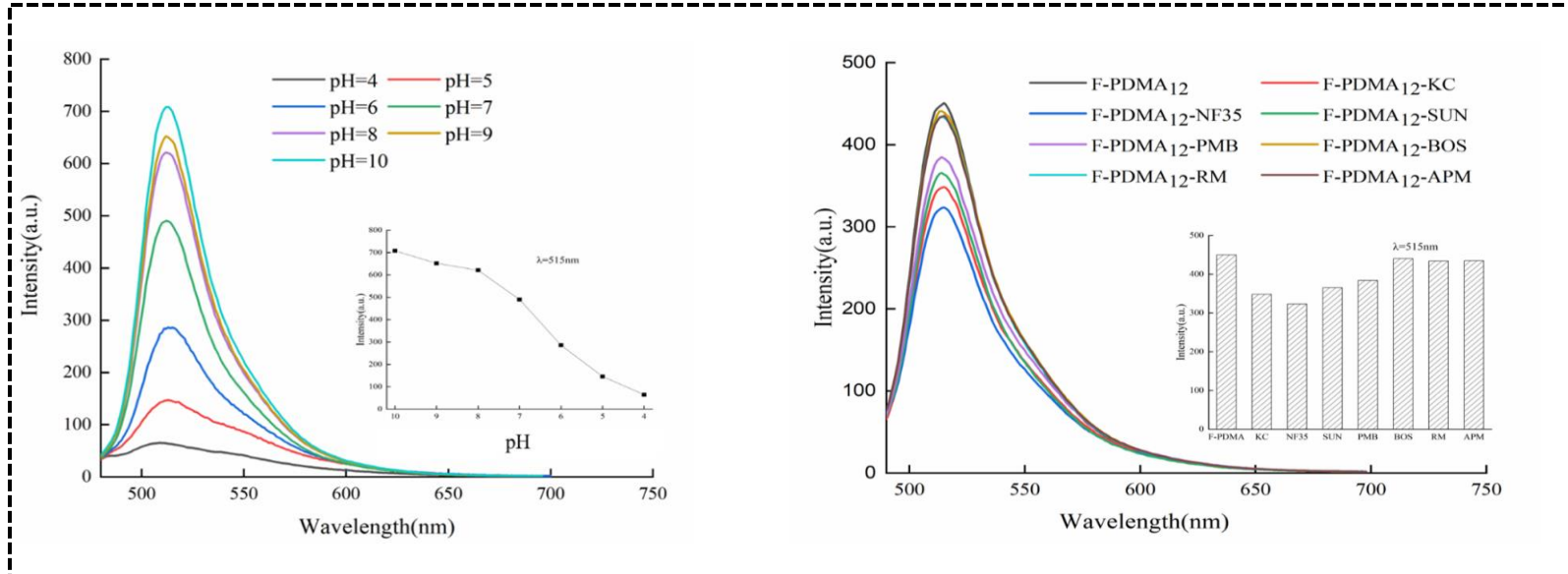
No.	Molar ratio of alcohol to MA	Thickening rate /%		Softness		Tearing strength (N/mm)		
		Ex	C	Ex	C	Ex	C	Δ
PDM-1	0.1:1	8.78	-0.52	3.25	4.08	85.14	78.46	8.51
PDM-2	0.2:1	9.67	1.34	3.37	4.17	93.73	85.79	9.25
PDM-3	0.3:1	12.08	-1.26	3.75	4.35	113.28	100.72	12.47
PDM-4	0.4:1	16.61	0.16	3.92	4.03	98.78	84.62	16.73

**The effect of the dosage of grafting agent on the yellowing resistance and fogging value of crust**

No.	Molar ratio of alcohol to MA	Yellowing resistance grade		Fogging value	
		Ex	C	Ex (mg)	C (mg)
PDM-1	0.1:1	3.5	2	3.17	4.50
PDM-2	0.2:1	4	2.5	3.57	4.62
PDM-3	0.3:1	3.5	2	2.98	3.71
PDM-4	0.4:1	3.5	2.5	3.27	3.87

- The introduction of dodecanol and DMEA into the polymer structure can significantly improve the softening ability of fatliquors.
- The softness, fullness and tear strength of green leather are improved.
- It exhibits better yellowing resistance and low atomization performance.

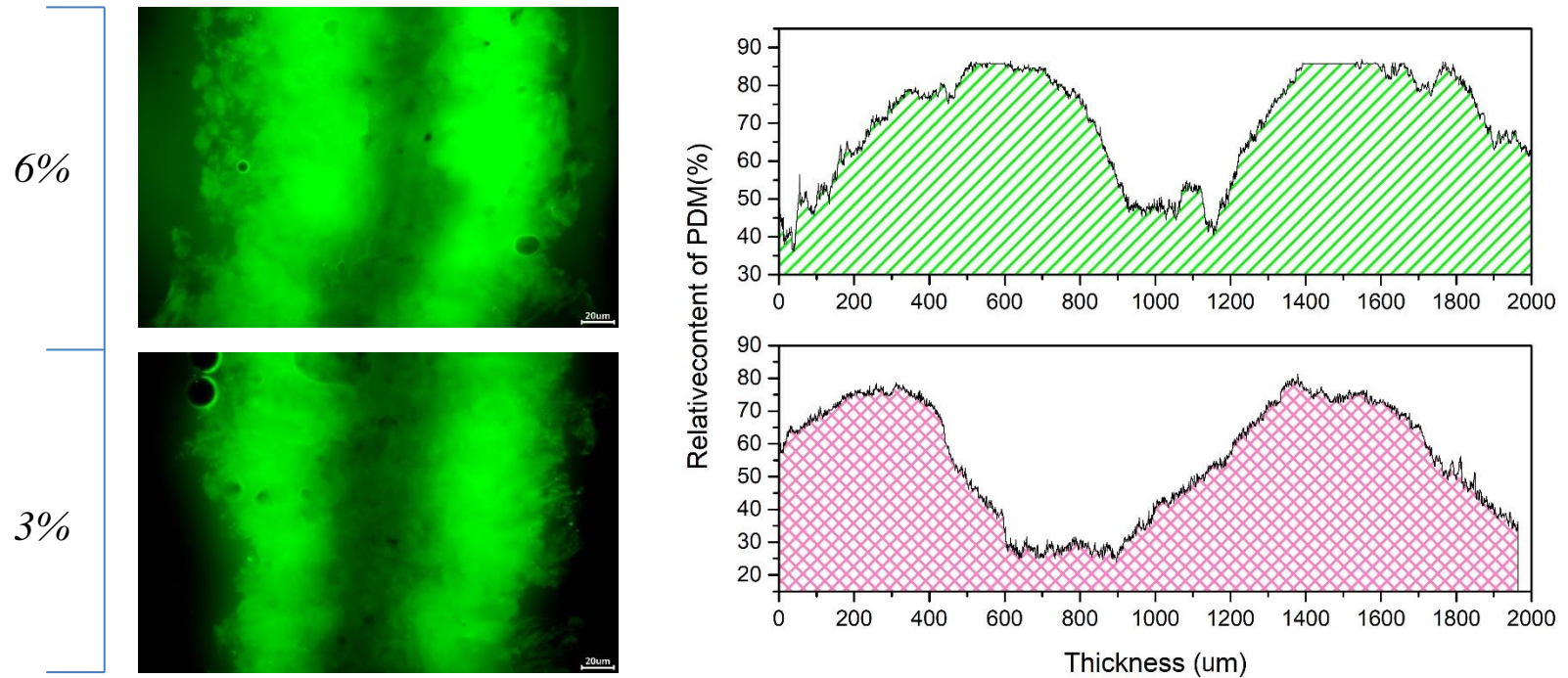
### 3. Mass transfer of F-PDM in the leather



#### *The fluorescence intensity of F-PDM*

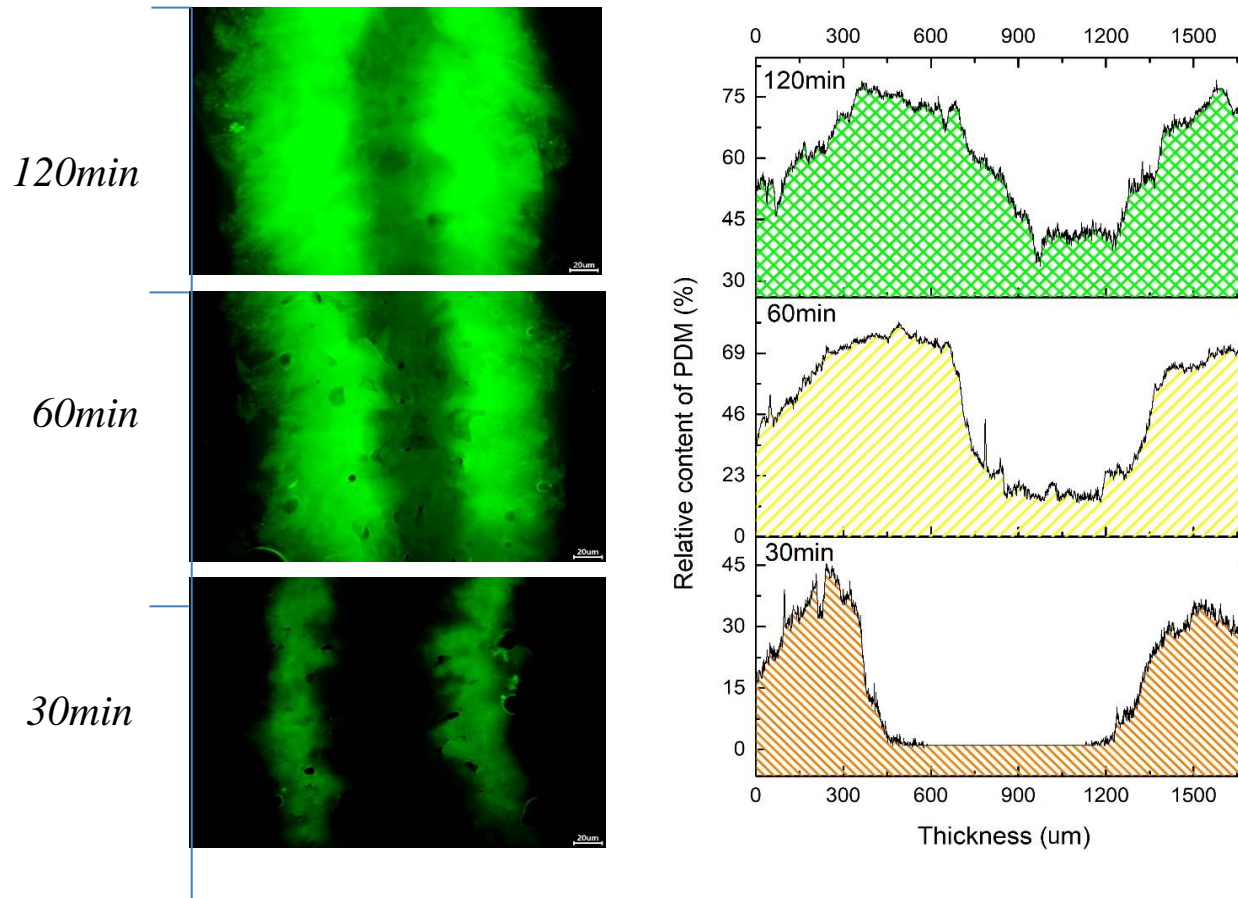
- The fluorescence intensity of F-PDM is responsive to pH.
- The fluorescence intensity was slightly reduced in the presence of seven leather auxiliaries.

### 3.1 The mass transfer of F-PDM



When the amount of F-PDM was less than 6%, the distribution of polymer fatliquoring agent in the center was slightly less.

## 3.2 The mass transfer of F-PDM



- Two sides of the second-layer leather penetration rate is basically the same.
- When the dosage of F-PDM was 6%, the infiltration of fat-adding agent could be completed within 120min



## 4. Conclusions & Outlook

- A new route for the preparation of polymeric fatliquor was proposed based on the *poly*(diisobutylene-maleic anhydride) (DM) as a platform.
- The fluorescence tracing technique of fatliquor established in this study can effectively analyze the mass transfer process and distribution state of fatliquor in the leather.



- We thank the National Natural Science Foundation of China (22078165) for supporting this research.



**Thanks!**