



# Mühendislik Fakültesi

## Kimya Mühendisliği Bölümü

***KMB256-Polimere Giriş***

***Dr. Öğr. Üyesi, İsa DEĞİRMENCI***

# Camsı Geçiş Sıcaklığına ( $T_g$ ) Etki Eden Faktörler

## ***KMB256-Polimere Giriş***

*Hafta-5*



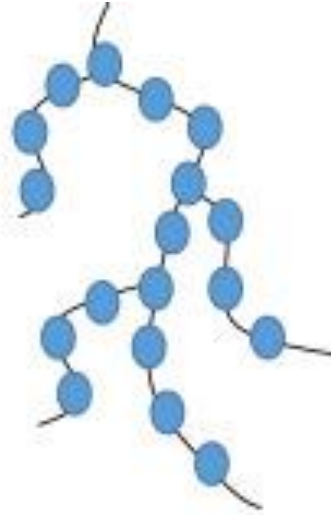
- A) Dallanma ve Çapraz bağlanma
- B) Yan grupların etkisi
- C) Polimer zincirlerinin esnekliği
- D) Hızlı yada yavaş soğutma işlemi
- E) Konfigürasyonel farklılıklar
  - Yapı izomerliği
  - Baş-kuyruk düzenlenmesi
  - Geometrik izomerlik
  - Taktisite
- F) Mol kütlesi



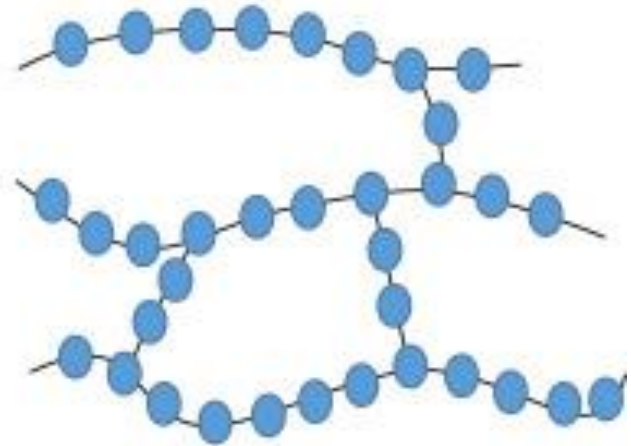
# a-) Dallanma ve Çapraz Bağlar



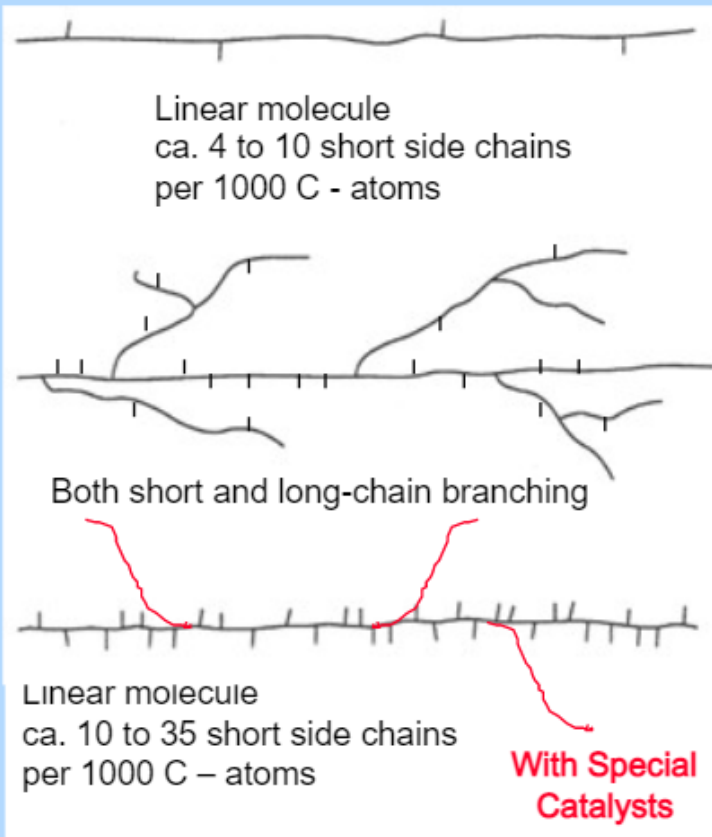
Linear polymer



Branched polymer



Crosslinked polymer

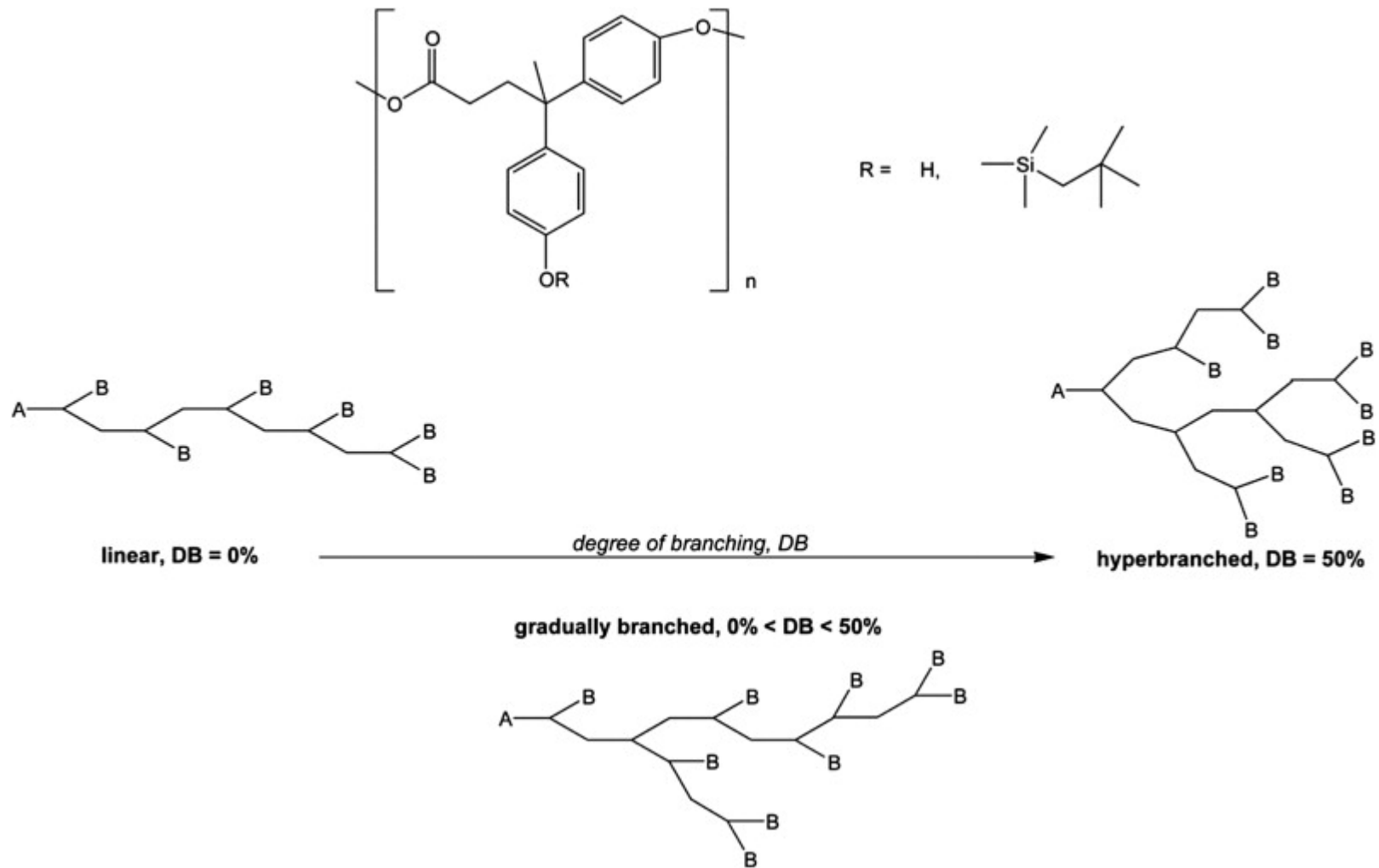


## Examples:

High-Density Polyethylene  
HDPE

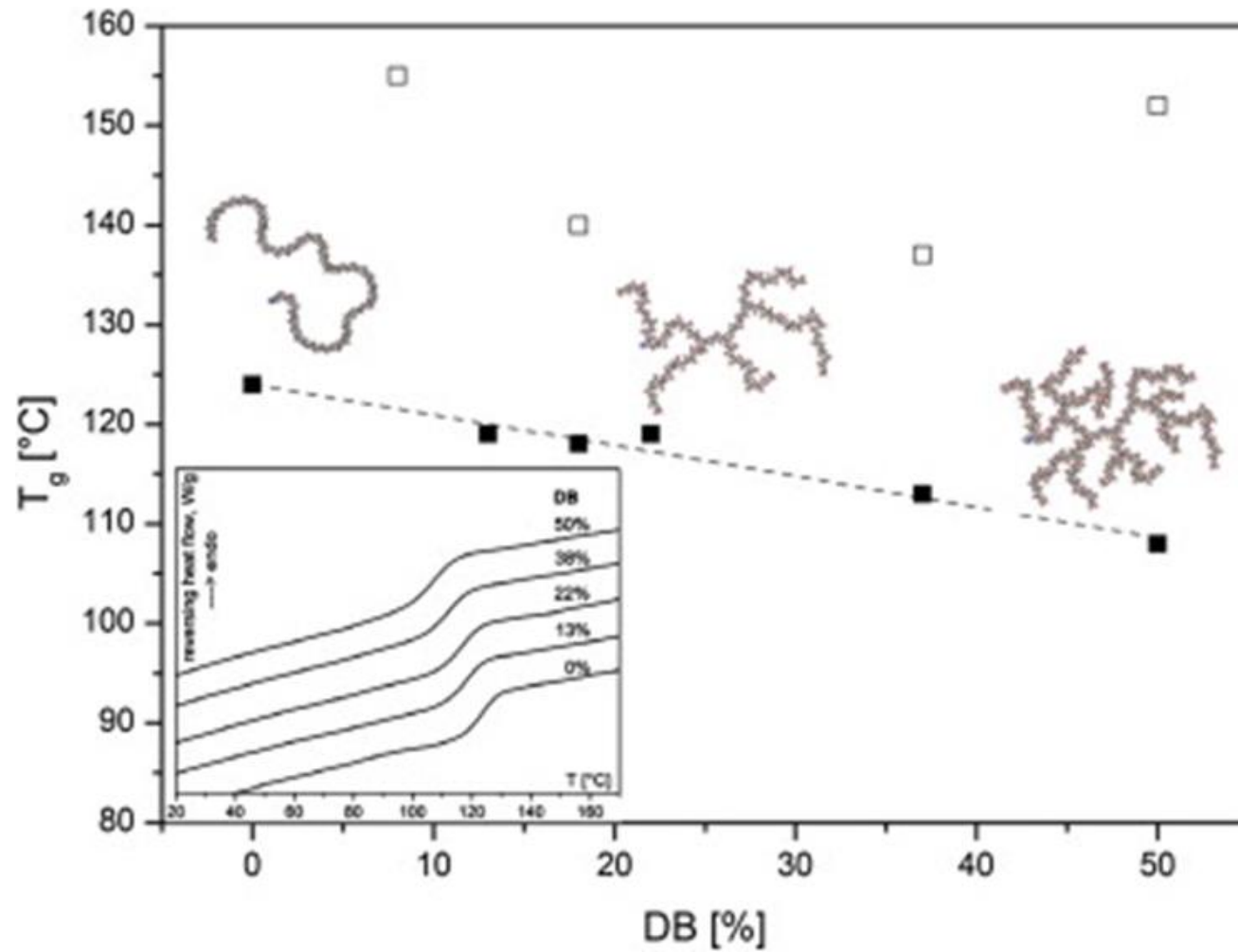
Very High Pressure  
Low-Density Polyethylene  
LDPE

Linear Low-Density  
Polyethylene - LLDPE

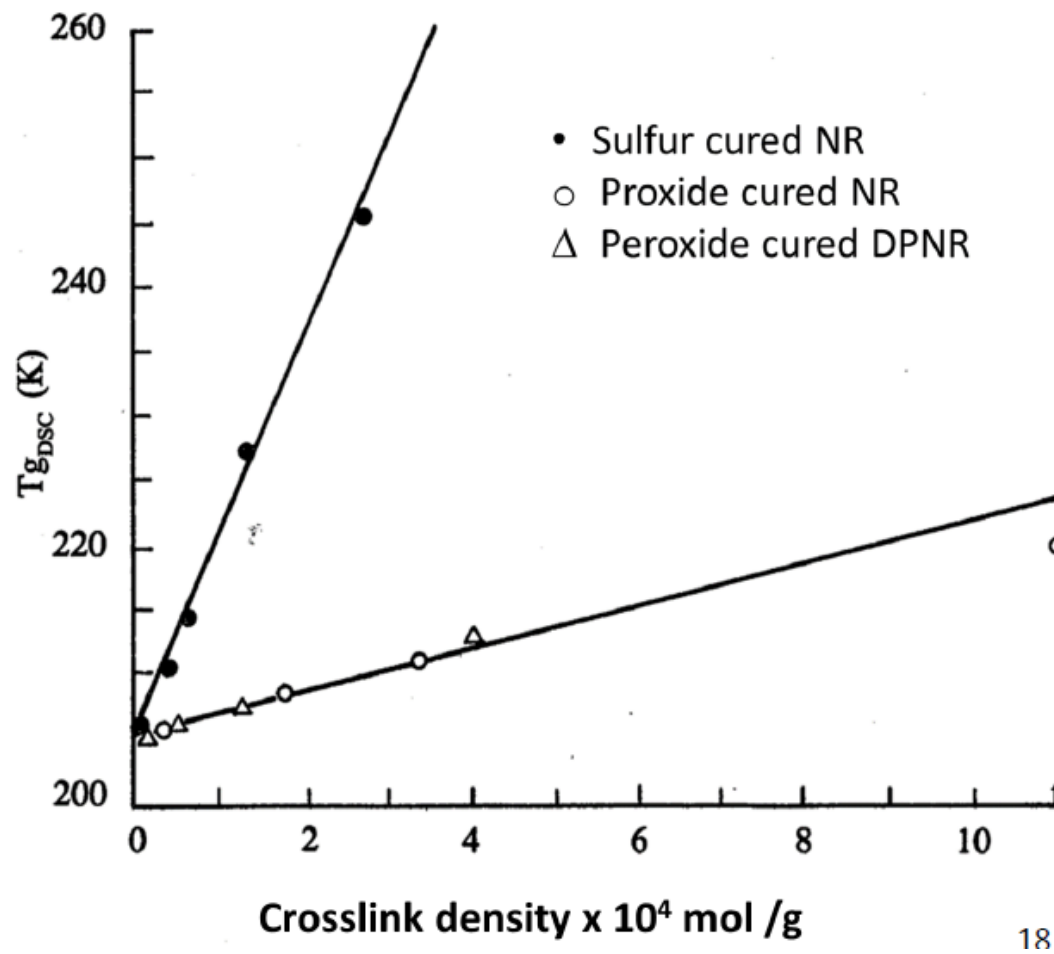


Alifatik-aromatik poliesterlerin dallanma dereceleri





# Çapraz bağlanma

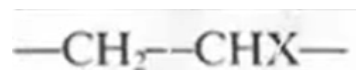


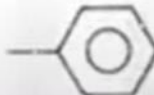
18





## b-) Yan Gruplar

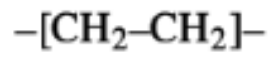


Side group (X)	T/K
$\text{—CH}_3$	250
$\text{—CH}_2\text{—CH}_3$	249
$\text{—CH}_2\text{—CH}_2\text{—CH}_3$	233
$\text{—CH}_2\text{—CH(CH}_3)_2$	323
	373
...	...

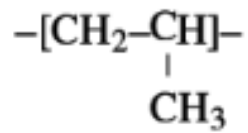
Pendant Side-Group	Tg (°C) <sup>a</sup>
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{—}$	-31
$(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{—}$	-14
$(\text{CH}_3)_3\text{CCH}_2\text{—}$	59

<sup>a</sup>Data from Stevens.<sup>4</sup>

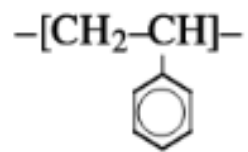




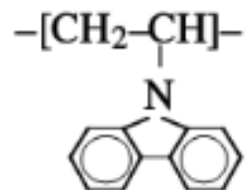
PE, polyethylene,  $T_g = -120\text{ }^\circ\text{C}$



PP, polypropylene,  $T_g = -15\text{ }^\circ\text{C}$

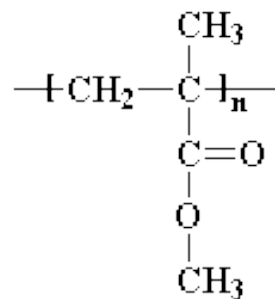


PS, polystyrene,  $T_g = 100\text{ }^\circ\text{C}$



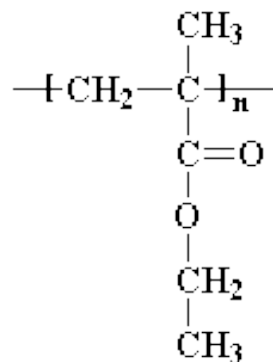
PVK, polyvinylcarbazole,  $T_g = 210\text{ }^\circ\text{C}$





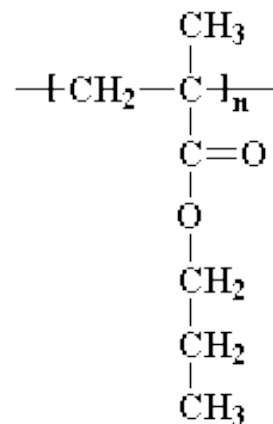
Poly(methyl methacrylate)

$T_g = 100\text{--}120\text{ }^\circ\text{C}$



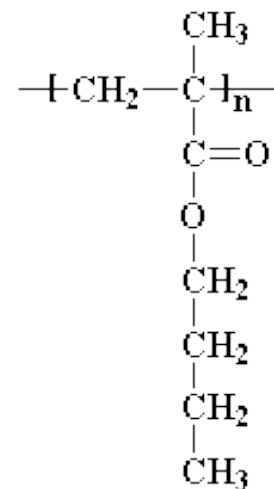
Poly(ethyl methacrylate)

$T_g = 65\text{ }^\circ\text{C}$



Poly(propyl methacrylate)

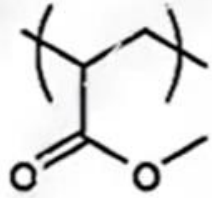
$T_g = 35\text{ }^\circ\text{C}$



Poly(butyl methacrylate)

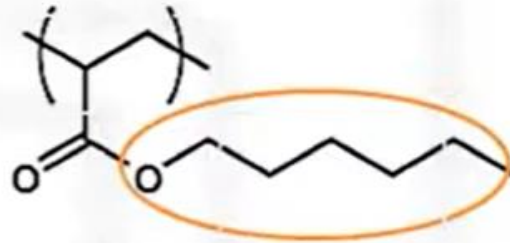
$T_g = 20\text{ }^\circ\text{C}$





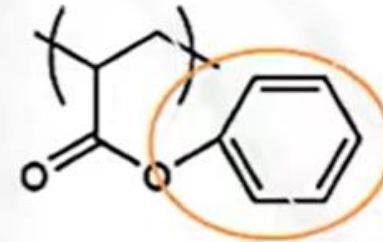
Arkadaki örnek gibi  
uzayan alkil grup  
plastikleştirci gibi görev  
görür ve  $T_g$  düşer

**Poly(methyl acrylate)**  
 $T_g = 10^\circ\text{C}$



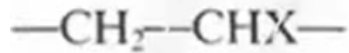
**Poly(n-hexyl acrylate)**  
 $T_g = -57^\circ\text{C}$

Fenilde durum başkadır  
iyi istiflenmeyi tetikler,  
sert gruptur.



**Poly(phenyl acrylate)**  
 $T_g = 57^\circ\text{C}$

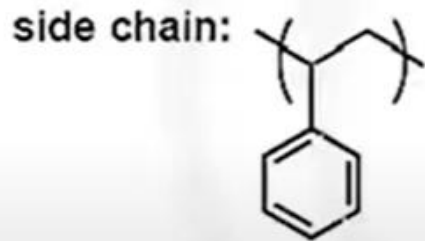
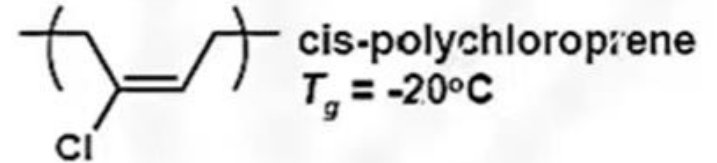
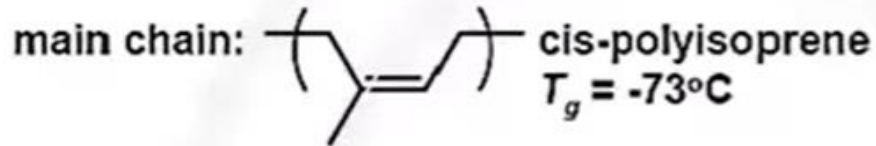
# Yan gruptaki polarite



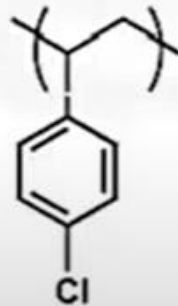
	Side group (X)	T/K
Polietilen	$\text{—CH}_3$	250
Polivinilklorür	$\text{—Cl}$	354
Polivinilalkol	$\text{—OH}$	358
poliakrilonitril	$\text{—CN}$	370



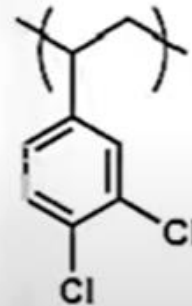
# Yan gruptaki polarite



$T_g = 100^{\circ}\text{C}$



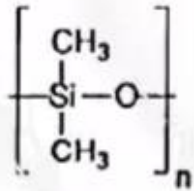
$T_g = 110^{\circ}\text{C}$



$T_g = 128^{\circ}\text{C}$

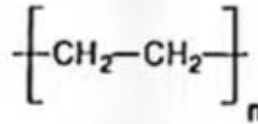
## c-) Zincir Esnekliği

Polimer omurgasındaki bağların dönmesi zorlaştıkça camsı geçiş sıcaklık artar



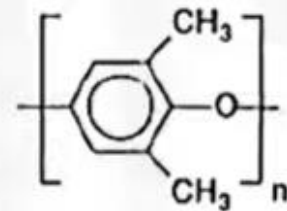
Poly(dimethyl siloxane)

$$T_g \cong -120^\circ\text{C}$$



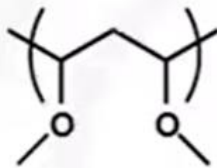
Polyethylene

$$T_g \cong -80^\circ\text{C}$$



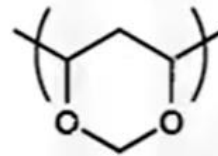
Poly(phenylene oxide)

$$T_g \cong +200^\circ\text{C}$$



poly(vinyl methyl ether)

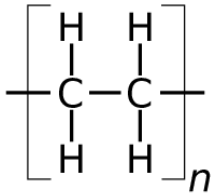
$$T_g = -13^\circ\text{C}$$



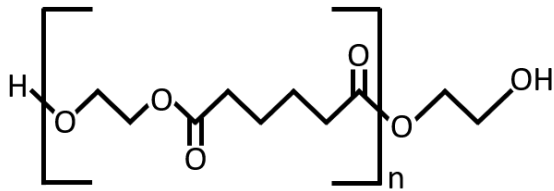
poly(vinylformal)

$$T_g = 105^\circ\text{C}$$

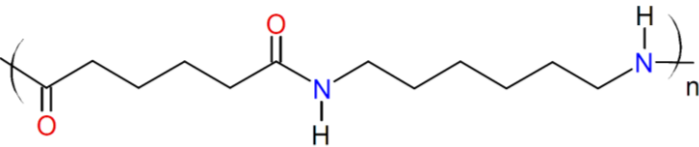
# Polar atomların ve hidrojen bağlarının varlığı



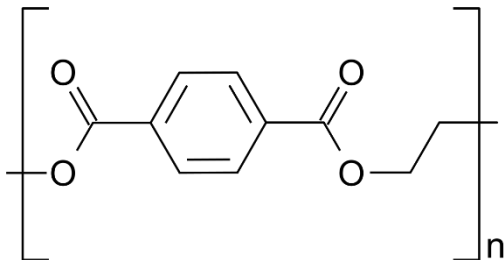
Polietilen,  $T_g = -115^\circ\text{C}$



Polietilenadipat,  $T_g = -70^\circ\text{C}$



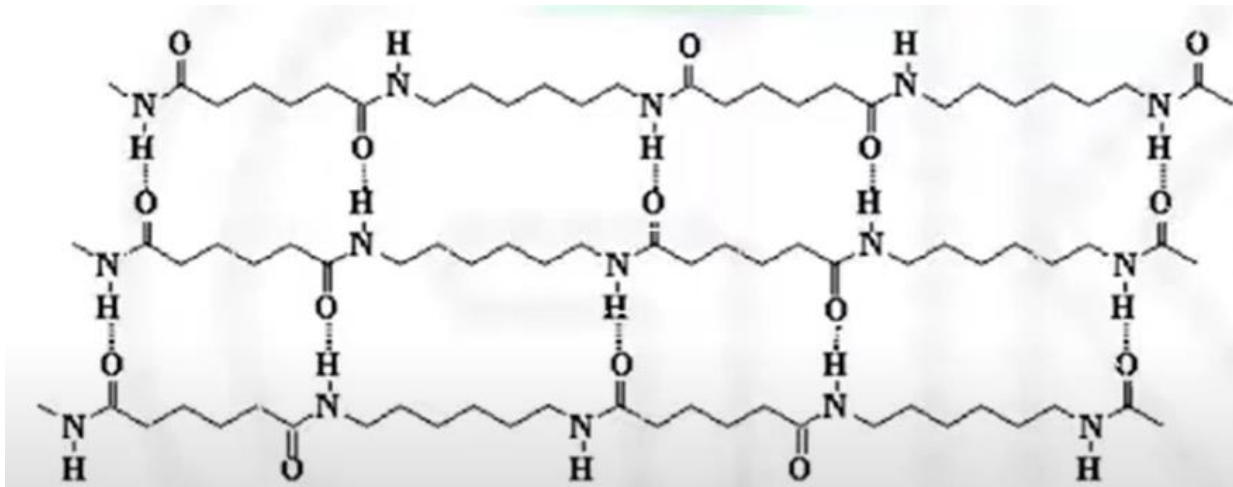
Poli(heksametilen adipamit),  $T_g = 50^\circ\text{C}$



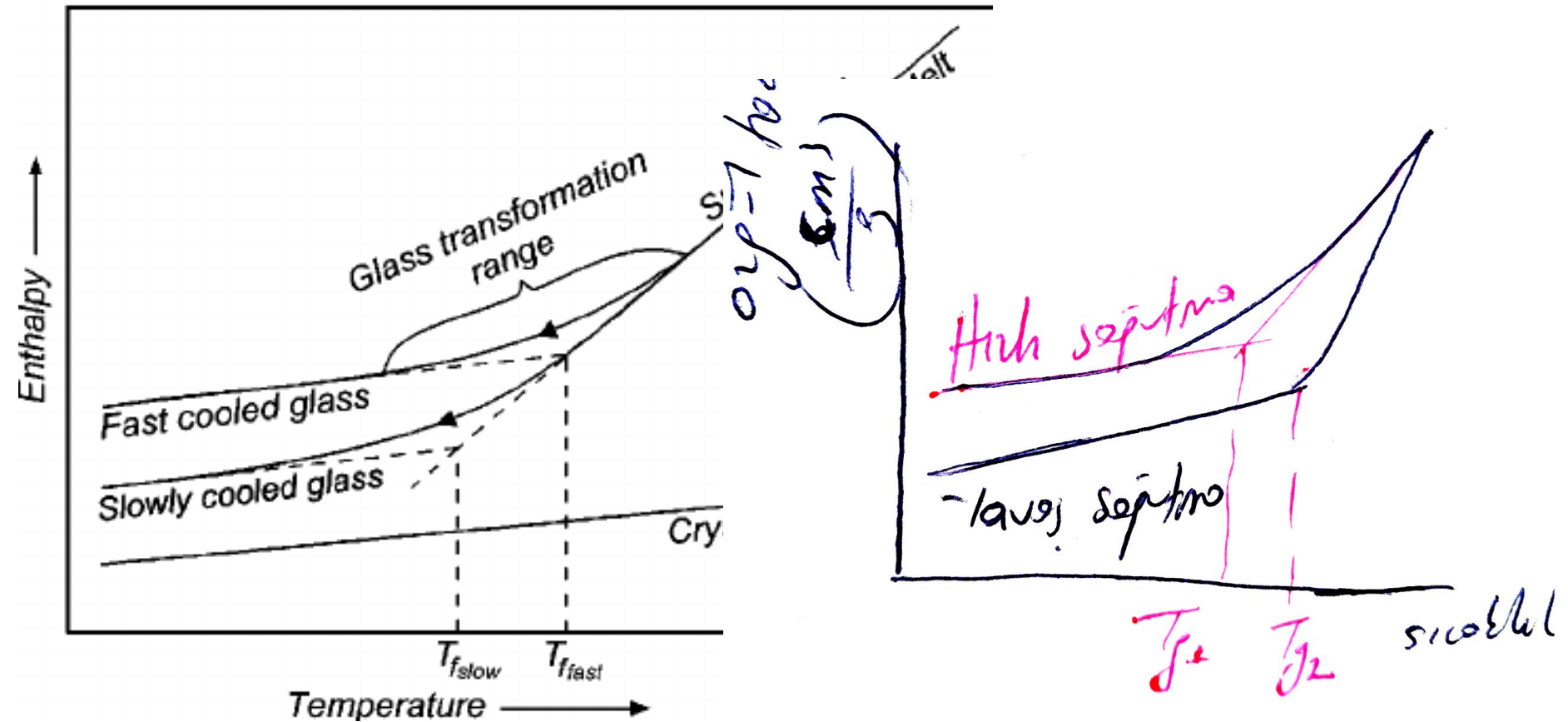
Poli(etilen teraftalat),  $T_g = 75^\circ\text{C}$







## d-) Hızlı Yada Yavaş Soğutma



# e-) Konfigürasyonel Farklılıklar

Yapı İzomerliği

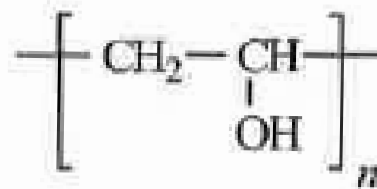
Baş-Kuyruk Düzenlenmesi

Geometrik İzomerlik

Taktisite



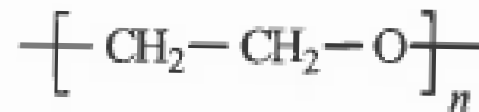
# Yapı İzomerliği



poli(vinil alkol)

$$T_g = 260\text{ }^{\circ}\text{C}$$

$$T_g = 80\text{ }^{\circ}\text{C}$$



poli(etilen oksit)

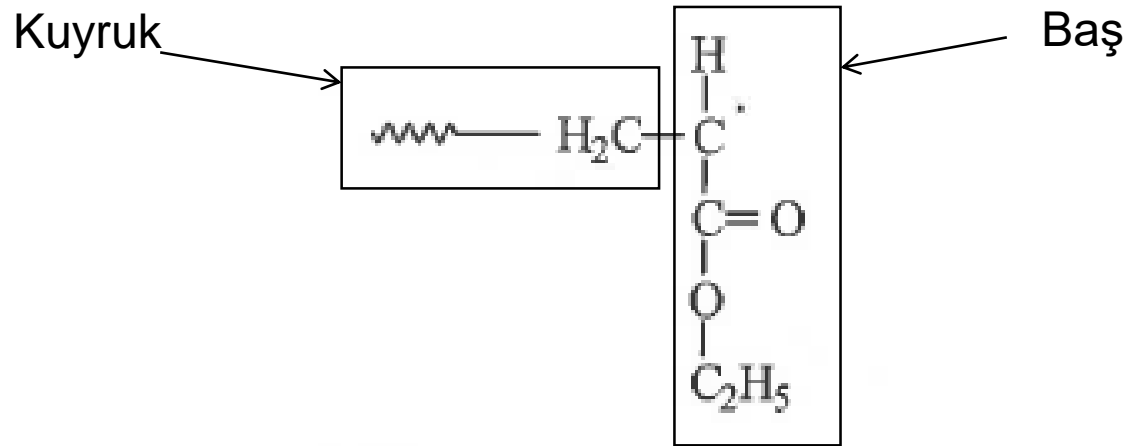
$$T_g = 60\text{ }^{\circ}\text{C}$$

$$T_g = -67\text{ }^{\circ}\text{C}$$

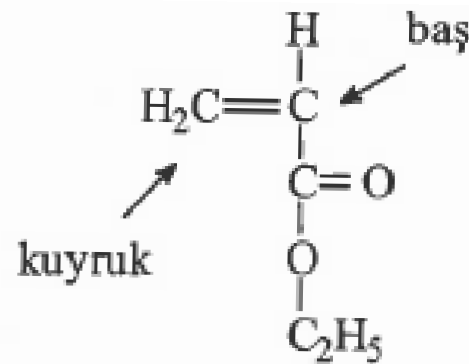
**İzomer** aynı kimyasal bileşime sahip olup, atomları arasındaki bağlantı yapıları farklı olan moleküller.

# Baş-Kuyruk Düzenlenmesi

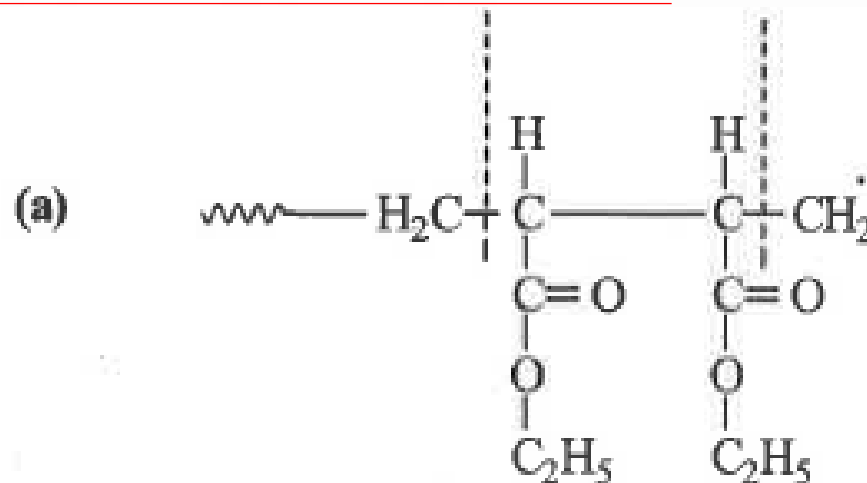
Baş-kuyruk veya kuyruk-kuyruk düzenlenmesine katılma polimerlerinde rastlanır. Etil akrilat monomerinin radikalik polimerizasyonu sırasında ortamda yapısı,



şeklinde gösterilebilecek aktif poli(etil akrilat) zincirleri bulunur. Etil akrilat monomerinin aşağıda gösterildiği gibi,  $-\text{CO}-\text{O}-\text{C}_2\text{H}_5$  grubunun bağlı olduğu karbon tarafı için *baş*, diğer karbonu için *kuyruk* tanımlaması kullanılırsa, yukarıda yapısı verilmiş olan aktif etil akrilat zincirine yeni bir etil akrilat monomerinin iki farklı şekilde katılma olasılığı vardır.

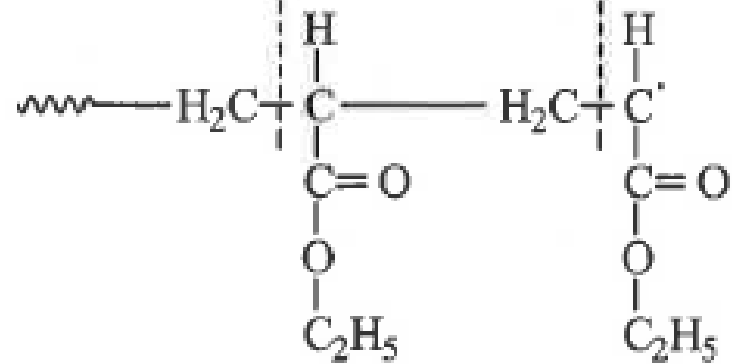


Birinci tür katılmada, etil akrilat molekülü zincire kendi  $-\text{CO}-\text{O}-\text{C}_2\text{H}_5$  grubunun bulunduğu karbon tarafından (baş) bağlanır. Katıldığı aktif etil akrilat zinciri de baş düzeninde olduğundan, bu tür katılma *baş-baş* katılması şeklinde adlandırılır. Baş-baş katılması sırasında *kuyruk-kuyruk* düzenlenmesi de kendiliğinden gerçekleşir (tersi de geçerlidir) (Şekil 2.6).



baş-baş katılması

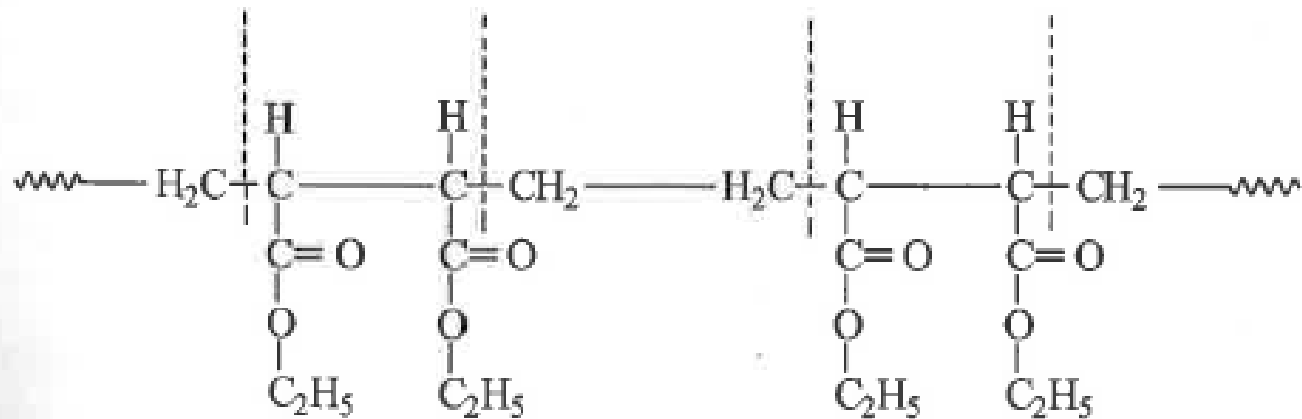
(b)



baş-kuyruk katılması

kuyruk-kuyruk katılması

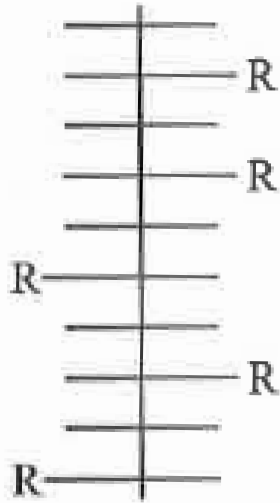
(c)



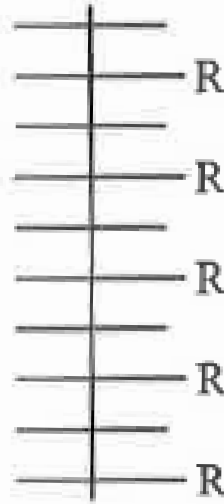
baş-baş katılması

baş-baş katılması

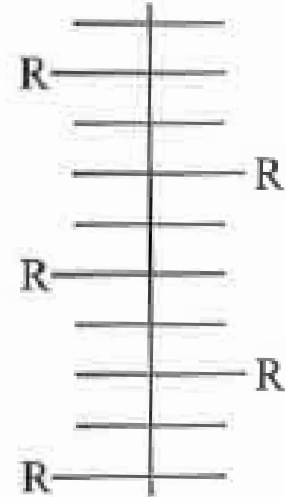
# Polimer Taktisitesi



ataktik  
(*ddl*dl...)

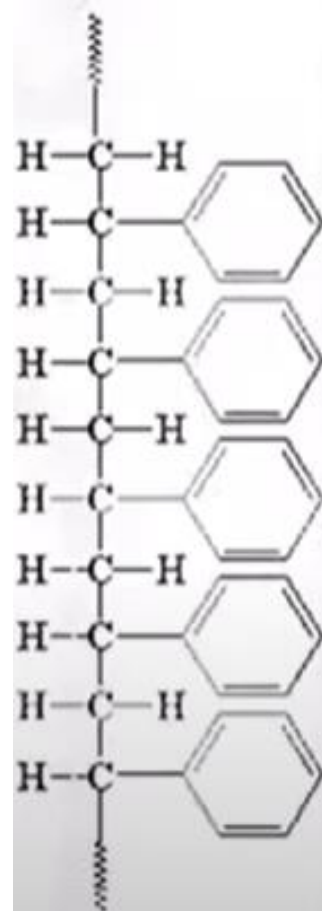


izotaktik  
(*dddd*d...)

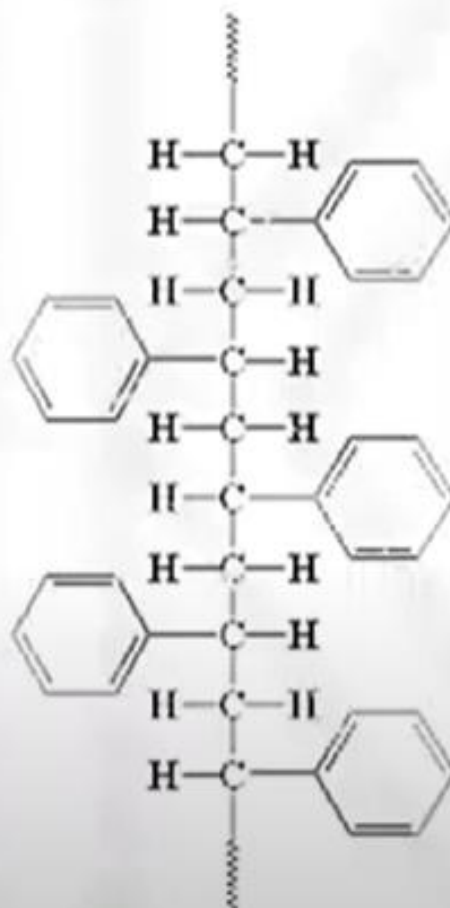


sindiyotaktik  
(*ldl*dl...)

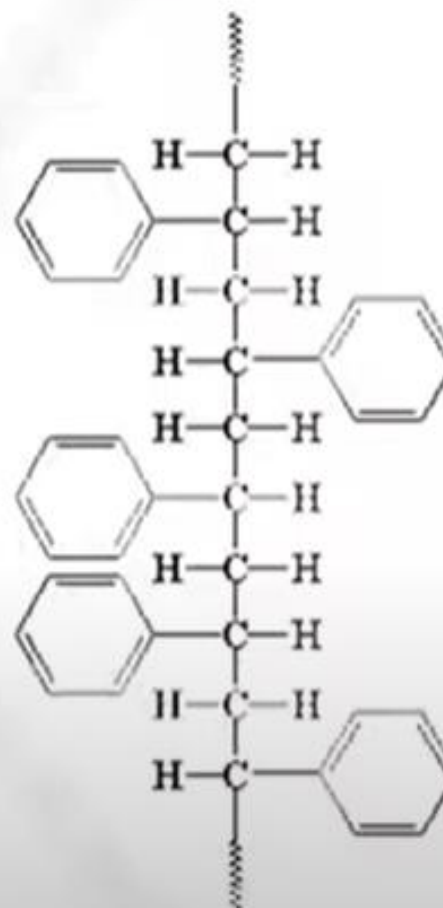




Isotactic

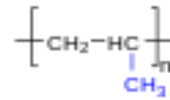


Syndiotactic

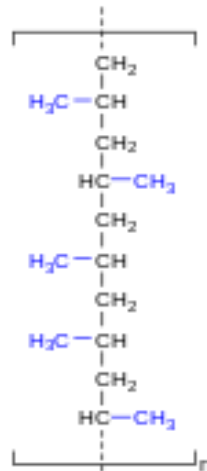


Atactic

## Polypropylen (PP)



### ataktisch (PP-at)

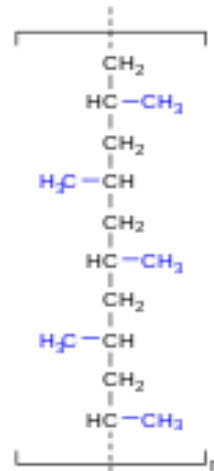


amorph

$T_g = -10\text{ }^\circ\text{C}$

$T_m = -$

### syndiotaktisch (PP-st)

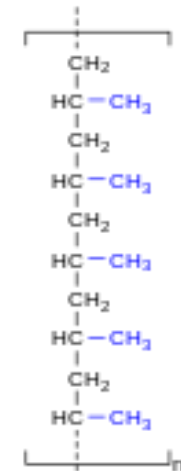


teilkristallin

$T_g = -8\text{ }^\circ\text{C}$

$T_m = 160\text{ }^\circ\text{C}$

### isotaktisch (PP-it)

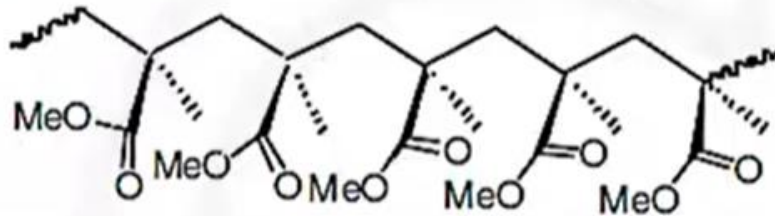


teilkristallin

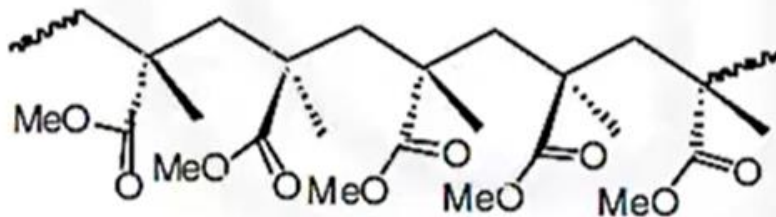
$T_g = 0\text{ }^\circ\text{C}$

$T_m = 184\text{ }^\circ\text{C}$

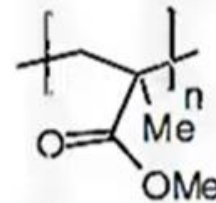




$T_g = 47\text{ }^{\circ}\text{C}$  (isotactic)



$T_g = 120\text{-}140\text{ }^{\circ}\text{C}$  (syndiotactic)

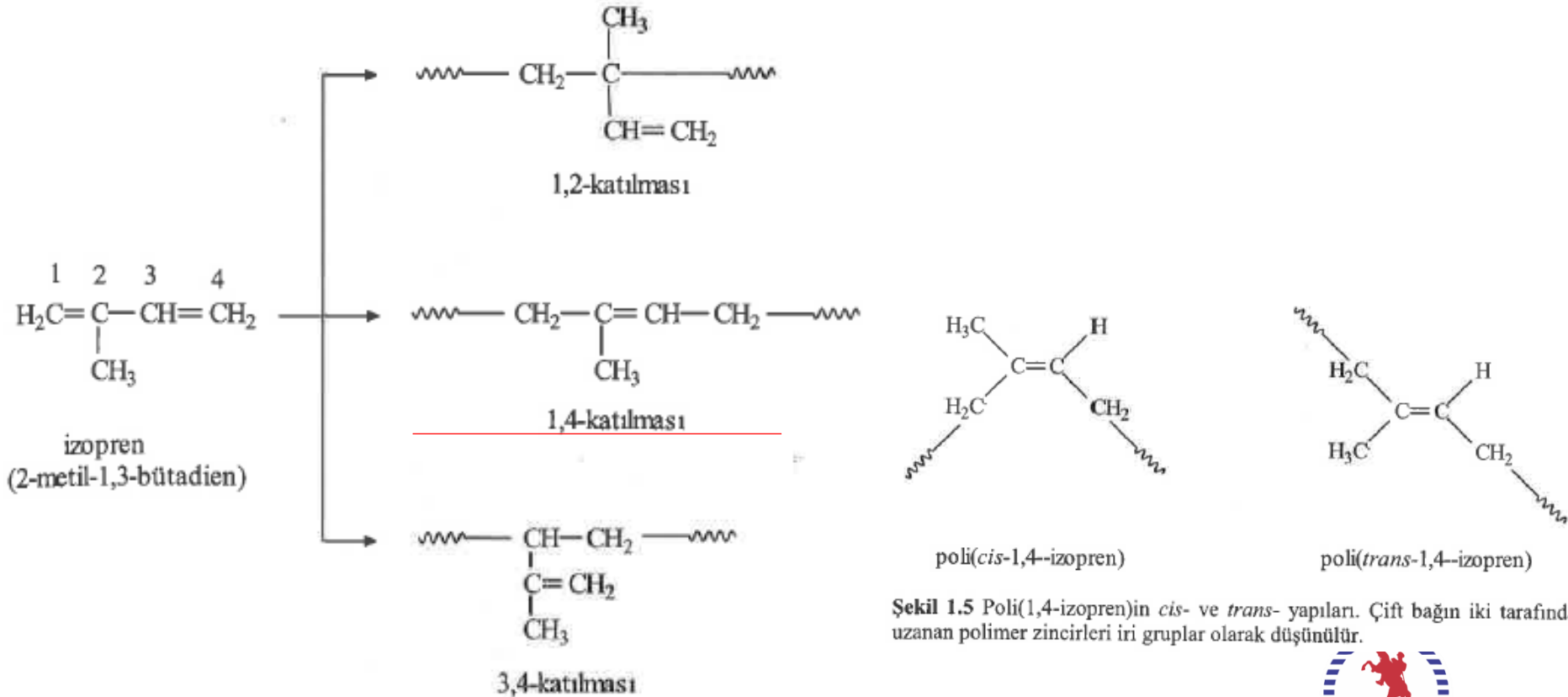


$T_g = 110\text{ }^{\circ}\text{C}$  (atactic > 50 % syndiotactic)

# Geometrik İzomerlik

Geometrik izomerlik (*cis*- veya *trans*- izomerliği) ana zinciri üzerinde çift bağ bulunan polimerler için geçerlidir.

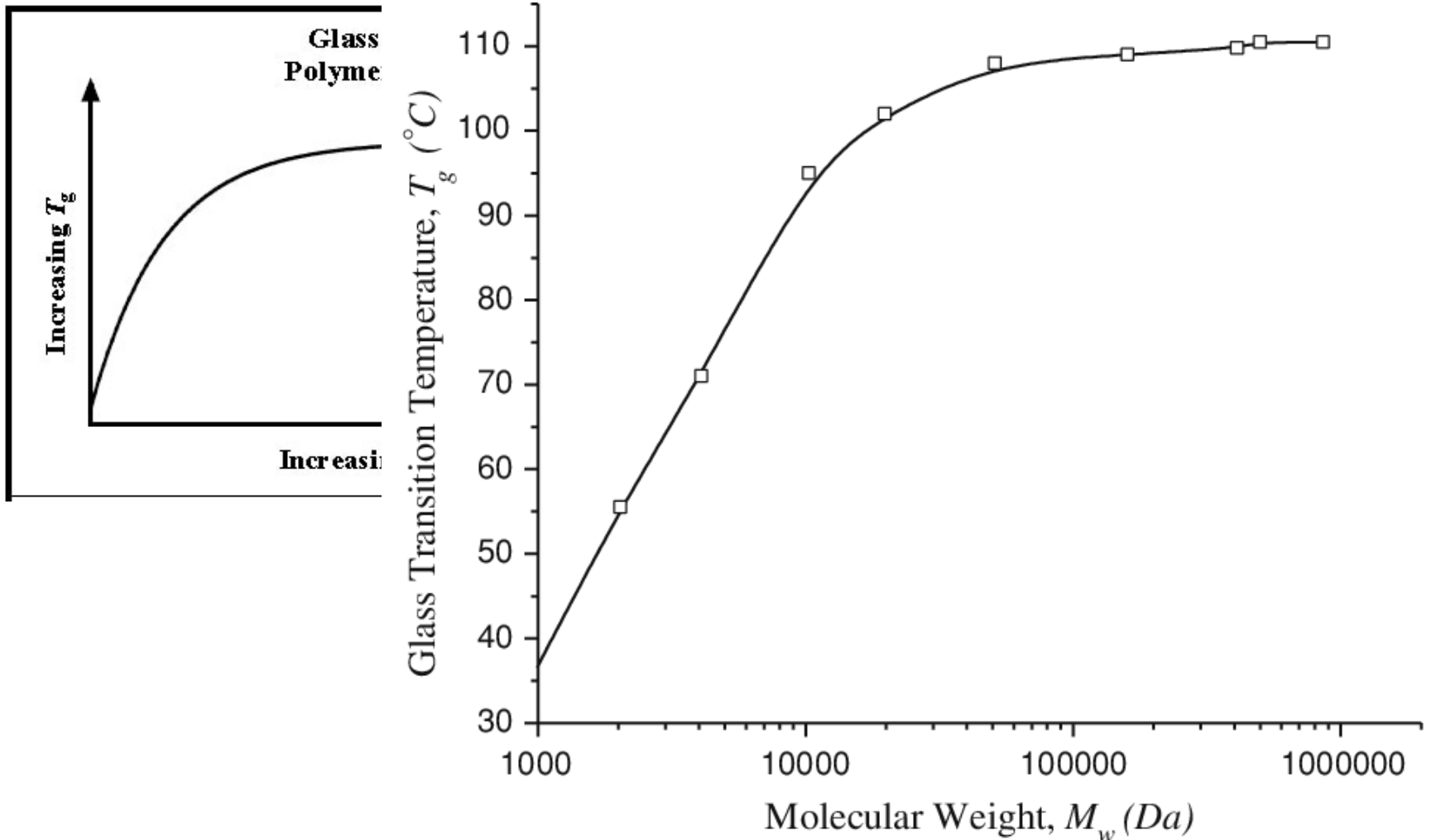
İzoprenin (2-metil-1,3-bütadien) polimerizasyonu sırasında Şekil 2.9 da yapıları verilen polimerlerle karşılaşılabilir. 1,2- veya 3,4-katılmasıyla elde edilen poliizoprenin ana zincirleri üzerinde çift bağ bulunmadığı için *cis*-, *trans*- izomerliği gözlenmez. Polimerlerin *cis*- veya *trans*- izomerliği değerlendirmesinde çift bağın iki tarafında uzanan zincir parçaları iri gruplar olarak düşünülür.



Şekil 1.5 Poli(1,4-izopren)in *cis*- ve *trans*- yapıları. Çift bağın iki tarafında uzanan polimer zincirleri iri gruplar olarak düşünülür.

Şekil 2.9 Poliizoprenin yapıları. 1,2- ve 3,4- katılmaları taktik polimer verir. 1,4- katılması ise geometrik izomerliğe yol açar.

## f-) Mol Kütlesi

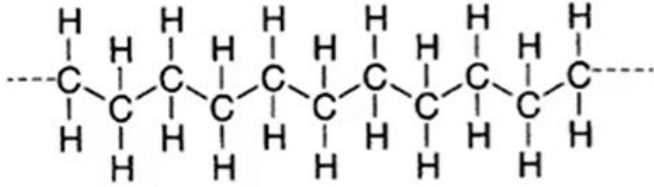


Polistiren'in camı geçiş sıcaklığına mol kütlesi değişiminin etkisi.

Petrol kaynaklı olan parafin farklı türlerde olabilmektedir.

## Gaz

4 karbon  
gaz



## Sıvı

5-6 karbon  
Sıvı

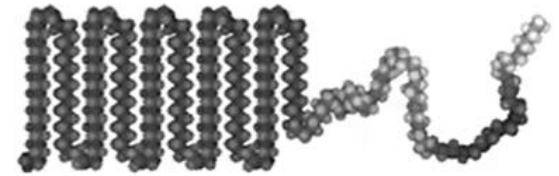
6-9 düşük viskoziteli sıvı

9-16 orta viskoziteli sıvı

## Katı

16-25 mumsu davranış  
çok yüksek vizkozite

25-50 arası karbonlu parafinler ise  
mumdur



Polimerizasyon derecesi artan polimerlerinde erime ve camsı geçiş (T<sub>g</sub>) değerleri değişim gösterir.

